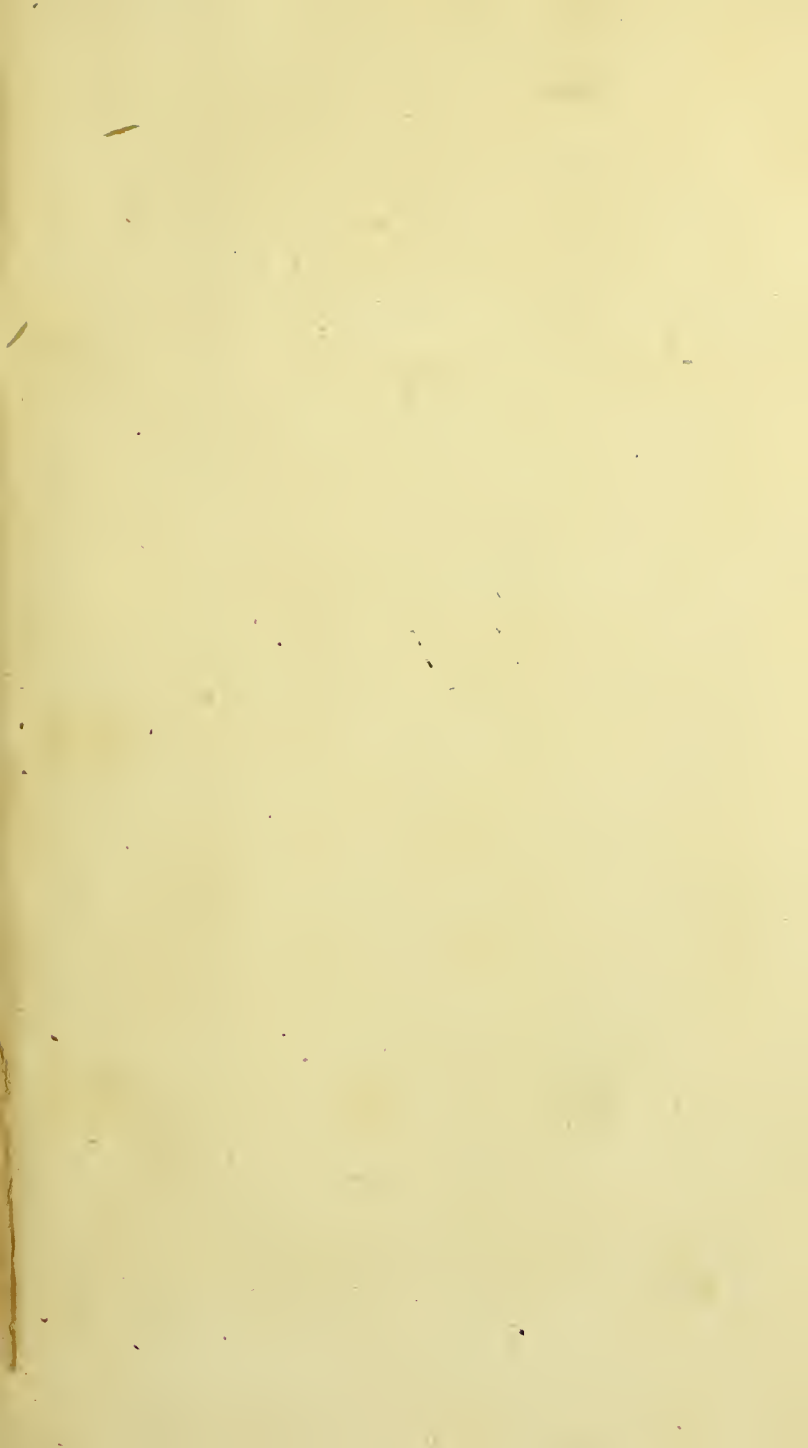



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ON  
CHEMICAL STATICS;

*Medican* WITH *Echnens*

COPIOUS EXPLANATORY NOTES,

AND AN

APPENDIX

ON

VEGETABLE AND ANIMAL SUBSTANCES.

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FAITHFULLY TRANSLATED FROM THE ORIGINAL FRENCH OF

C. L. BERTHOLLET,

MEMBER OF THE CONSERVATIVE SENATE, OF THE INSTITUTE, &c.

By B. LAMBERT:

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IN TWO VOLUMES.

VOL. II.

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LONDON:

PRINTED FOR J. MAWMAN, 22, POULTRY.

1804.

W. Flint, Printer, Old Bailey.

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~~Handwritten scribble or signature~~

4. 12. 20

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AN  
E S S A Y  
ON  
CHEMICAL STATICS.

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PART THE SECOND.

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*Of the Chemical Action of different Substances,  
and of the Phenomena dependent on it.*

257. HAVING successively examined all the causes which contribute to chemical phenomena, independently of the particular character of the substances in which they exist; I purpose, in the second part of this work, to consider the substances themselves, whose properties are the real powers which produce the effects of chemical action.

It follows, from the considerations set forth in the first part, that the forces which substances can develop in their action depend, 1st, on their tendency to combination, by which a saturation is produced; or in their affinity for other substances, which may be called the affinity of combination:

2d, on the reciprocal affinity of their *moleculæ* before combination, or of those of the integrant parts of the combination : to this affinity may be assimilated that of those substances which do not occasion a mutual saturation of their characteristic properties, but whose effects are analogous to those of the reciprocal affinity of the *moleculæ*. When this reciprocal action is sufficiently energetic, it produces the force of cohesion, by which name I have frequently designated it.

I shall therefore trace the changes which these two causes of the chemical action of different substances experience in the combinations which they form, at the same time endeavouring to derive the properties of the combination itself from the primitive properties of its elements.

I shall distinguish the substances which exercise a simple affinity, independent of all composition, from those which, in some circumstances, exercise a resulting affinity, similar to the preceding, and which, on other occasions, act by their elementary affinities : I shall follow the changes arising from the condensation which gives birth to the resulting affinities, as well as those which supervene when it yields to the elementary affinities.

Caloric concurs with the chemical forces of substances, by the unequal elasticity which it gives to them : it is in opposition to the force of cohesion, and to every species of combination in which the approximation of the parts is essential ; nevertheless, as its effects unite with those of the affinity of combination,

bination, and of the reciprocal affinity, it sometimes becomes an obstacle to combinations, and sometimes it favours them. I shall examine the dispositions of substances in these different views; in general I shall notice the connection of the properties of the substances with the effects which they produce; sometimes I shall consider the phenomena, to show the different causes from which they are derived.

There are predominant affinities in substances which are the source of their characteristic properties (37); there are others which are inferior to these, but which nevertheless give rise to several remarkable phenomena: the first are chiefly useful in the classing of substances, and in explaining the principal effects resulting from their action; but the others must not be neglected. Thus, proceeding to the substances whose affinity for oxygen is that which predominates, I shall examine their mutual combinations.

I shall not carry the plan I have traced into execution with the minuteness of a treatise on chemistry: I shall only examine those substances which are eminent for their properties, whose action explains that of analogous substances, and which are the powers that particularly engage the attention of the chemist; or, at least, I shall only point out the others by their differences.

I suppose myself in a situation in which I recall to a student the objects that have passed under his observation, to show him the connection which exists between the particular properties and the

general properties ; between the simple phenomena and the compound phenomena ; between the dispositions of substances and the processes to which they are submitted : I examine with him those opinions which are not yet established : I discuss the knowledge, still vague, which forms what may be called *floating* chemistry : but these discussions, and the conjectures to which they have led me with respect to objects on which I have formed any particular opinion, I submit to chemists.

## SECTION I.

*Of Oxigenable Substances, considered in their Relations with Oxygen, and in their mutual Relations.*

## CHAP. I.

*Of Oxygen and Oxigenation.*

258. WITH the exception of caloric, oxygen seems to take the lead of all substances by the extent and energy of its affinities; by its action on caloric, it also contributes the most to those phenomena which are dependent on its combination.

Oxygen not only enters into combination with a great number of substances, but the tendency which these have to combine with it generally forms their distinctive character, which they retain, more or less, in their mutual combinations; so that the relation of the different substances with oxygen must particularly direct their chemical classification, and serves principally for the explanation of the phenomena to which they contribute. Before entering into an examination of the particular combinations which oxygen forms, and of the substances with which it produces them, I shall



I shall apply to it, the general observations which I have offered on the combinations of gaseous substances, either with each other, or with substances which are in another state.

The properties of oxygen receive considerable modifications in its combinations, according to the state of condensation in which it is found; according to the quantity of caloric which it retains in them; and according to the degree of saturation it experiences; so that by passing successively into different combinations, it can give them different properties with respect to the state in which it is found in them.

By its condensation it carries a much more considerable mass into the sphere of activity, and its action is increased in proportion to its state of condensation: but it only retains that part of its tendency to combination which is not subdued by the affinity of the substance with which it is combined: hence it loses more of its own properties in proportion as the substance with which it is combined has a stronger affinity for it, and is in greater quantity in the combination (180).

As it has a great disposition to elasticity, every elevation of temperature weakens its combination with solid bodies, and in general with every substance in which this disposition is less; consequently the lower the temperature is, the greater force must this species of combination have: and if heat is necessary to the combination of oxygen with solids, it is because it promotes it more  
by



by diminishing their force of cohesion, than it hinders it by the dilatation of the oxygen (153).

In the condensation which oxygen experiences by combination it does not lose a quantity of caloric corresponding with the condensation (147); but it retains more or less, according to the resulting force which the combination exercises on the caloric, and which can only be determined by experiment: hence, the different phenomena occasioned by caloric, when oxygen passes from one combination to another.

259. A judgment may be formed of the action of a substance on oxygen, by the properties of the combinations which it forms with it, and in which those of the oxygen have experienced a greater or less saturation (183); but to be enabled to compare substances with each other, in this respect, the proportions of the elements in the combinations formed with the oxygen must be known; regard must be had to the state of condensation in which it is found in them, and a just idea must be formed of the properties which may depend on it. Now, the two properties which particularly characterise oxygen, are 1st, that of combining with substances which are inflammable, and which cease to be so by the combination: 2nd, that of communicating acidity to the combinations which it forms, when it does not experience too great a degree of saturation: in this latter view, it was right to call it the acidifying principle.

On other occasions I have resisted this latter  
idea,

idea, for which we are indebted to Lavoisier, but, at present, it appears to me that too much latitude has been given to the principle it was intended to establish, while, on my side, I have restricted it too much.

In fact, it is carrying the limits of analogy too far to infer that all acidity, even that of the muriatic, fluoric, and boracic acids, arises from oxygen, because it gives acidity to a great number of substances.

Sulphurated hydrogen, which really possesses the properties of an acid, proves, directly, that acidity is not, in all cases, owing to oxygen.

There is no better foundation for concluding that hydrogen is the principle of alkalinity, not only in the alkalis properly so called, but also in magnesia, lime, strontian, and barites, because ammonia appears to owe its alkalinity to hydrogen.

On the other hand, the objection which I rested on the properties of oxygenated muriatic acid, which the oxygen seems to deprive of acidity, does not appear to me to be founded, because I overlooked the state in which it exists in it.

The oxygen is but feebly retained in oxygenated muriatic acid, so that it easily abandons the muriatic acid, especially to combine with condensed hydrogen; this soon gives rise to the decomposition of the oxygenated muriatic acid; but it really enters into combination with the alkalis, for I am convinced that by mixing an  
alkali

alkali or an alkaline earth with it, its natural properties were diminished, and its odour, very much weakened, shows it clearly; but it only acts on the alkalis as a weak acid, because it is but little condensed, and the objection which is drawn from the debility of its action in this case, is also applicable to muriatic acid whose action on the alkalis is equally weak; nevertheless in proportion as it is concentrated it acquires force, and drives the carbonic acid from its combinations with pot-ash and soda, although this has a considerable capacity for saturation: its action on muriatic acid also augments by its condensation, and this reciprocal saturation must weaken their tendency to other combinations: in the super-oxygenated muriate of pot-ash, in which the oxygen is much more condensed, and in a much greater proportion than in oxygenated muriatic acid, it saturates a considerable portion of pot-ash, by acting on it with a resulting affinity.

These considerations prove that oxygen may be regarded as the most usual principle of acidity, but that this species of affinity for the alkalis may belong to substances which do not contain oxygen; that we must not therefore always infer from the acidity of a substance that it contains oxygen, although this may be an inducement to suspect its existence in it, still less should we conclude because a substance contains oxygen that it must have acid properties; on the contrary, the acidity of an oxygenated substance shows that

that the oxygen has only experienced an incomplete saturation in it, since its properties remain predominant.

260. When therefore a substance combines with oxygen, we must determine the proportion of it which enters into the combination, and examine the properties of this combination: strong affinity for it may be attributed to those substances which can vanquish, and combine with a large quantity of it without becoming acids, and without showing such other dispositions to combination as belong to oxygen.

This method of judging of the comparative affinity of different substances for oxygen is the same as that by which the comparative capacity of acids and alkalis for saturation is determined (88), and appears to me to be applicable to all the affinities of combination.

The simple or undecomposed substances on which oxygen exerts a powerful action, and with which it forms the most remarkable combinations, are hydrogen, carbon, sulphur, phosphorus, azote, and metallic substances: the latter substances, with the combinations they produce, and the phenomena derived from them, shall be particularly examined; among the others, hydrogen and carbon are those which, in this respect, hold the first place.

Of all the known substances, there is not any of which an equal weight can combine with so large a proportion of oxygen, covering, at the same time, its

its characteristic properties, as hydrogen, but losing also all those which characterise itself: it requires only about  $\frac{1}{16}$  of hydrogen, to saturate nearly  $\frac{8}{16}$  of oxygen, to this point.

I have shown that it is at the term at which the effect of the most powerful reciprocal action, and consequently the condensation, is greatest, that the combination of two gaseous substances can be effected (206): so great an effect of saturation, which is unexampled in chemical combinations, proves a great power of action in hydrogen; it ought therefore to be considered as much more active than oxygen, if it exercised a correspondent action on a sufficiently great number of substances; but there are several with which it only forms weak combinations, and a still greater number with which it does not form any, because the weakness of its action on these substances cannot overcome the obstacles which oppose its union with them; besides, it has much less relation with caloric than oxygen: these motives should engage us to class and examine the different substances, principally, according to their relations with oxygen.

261. Hydrogen, whose specific gravity in the state of gas is nearly as 13 to 1, contributes to the specific lightness, and to the volatility of all the substances in which it is combined; it particularly gives the property of inflammability to its combinations, which is owing to its predominating affinity with oxygen.

Elevations



Elevations of temperature diminish the condensation produced by combination, and consequently the effect of the reciprocal affinity of its elements: the energy of the affinity weakens therefore in proportion as the temperature is raised, and when it reaches the term at which the dilatation produced by heat counterbalances the condensation produced by the affinity, the force of the combination will be greatly weakened.

It is probably by producing a similar effect, that a strong electricity decomposes water, when this decomposition is not limited to the disengagement of a part of one of its two elements; as in the action of the electromotive apparatus (139).

This action of electricity, analogous to that of heat, seems therefore to prove that there is a degree of temperature at which water cannot exist, but in which it is reduced to its two elements, which separate, as takes place with ammonia at a much lower degree: the substances which decompose it by simply disengaging the hydrogen gas, only accelerate the term of this natural separation, as those which decompose ammonia by carrying off its hydrogen, accelerate that at which heat alone would have produced its separation.

If a substance, iron, for example, acts on the oxygen of water, at the same time that this experiences a dilatation which weakens the reciprocal action of its elements, its action concurs with that of the heat: but this effect must have its limits,



limits, because a high temperature tends also to separate the oxygen from the iron.

The decompositions produced by a concurrence of circumstances which change the mutual action of the different substances, may easily occasion errors with respect to the comparative affinity of these substances; thus, it must not be concluded, because iron decomposes water, that it has a stronger affinity with oxygen than the hydrogen, for this decomposition is only effected by means of the dilatation which the hydrogen gas experiences from the action of heat; and in a different circumstance, the hydrogen takes the oxygen from the iron, notwithstanding the disadvantage with which a very rare substance exercises an action opposite to that of a condensed substance.

Priestley has shown that by directing the focus of a burning-glass on oxide of iron, in a jar filled with hydrogen gas; the metal was completely reduced: in this case, the hydrogen gas undergoes little change of temperature, and little augmentation of its elastic effort; but the oxygen experiences a very considerable one, and abandons the iron to combine with the hydrogen, from which it would, on the contrary, have been separated by the iron, if the effect had been the same on both, as in the decomposition of water. (*Note XIX.*)

262. Carbon also exercises a powerful action on oxygen; nevertheless it requires nearly 16 ponderable parts to be able to subdue 43 of oxygen, and the combination then formed is a powerful acid: the  
carbon,

carbon, in this proportion, is only capable of saturating part of the properties of the oxygen; it appears, therefore, that its affinity is much inferior to that of hidrogen.

Several complicated phenomena arise from carbon having, at the same time, a great affinity for hidrogen; so that it easily forms gaseous combinations with it, and always retains it in combination, while it preserves the solid state: it has, besides, the property of forming ternary combinations with oxygen and hidrogen: from all that can be drawn from the experiments hitherto made on this remarkable substance, it is only in the diamond that it is yet known, in an insulated state.

A proof of the stronger action of hidrogen on oxygen is, that at all temperatures, those substances which contain carbon and hidrogen yield water rather than carbonic acid, unless a triple combination is formed; so that inflammable substances begin by being converted into charcoal, that is to say, they commence by giving up their hidrogen, losing at the same time their other volatile principles. An elevation of temperature weakens the reciprocal action of oxygen and hidrogen, but it weakens still more that of carbon, which is much less dilatable than hidrogen: thus we see that hidrogen decomposes carbonic acid.

The decomposition of water by charcoal is not owing to a superiority of the affinity of carbon for the oxygen: in this case, two combinations  
are

are formed, that of carbonic acid, and that of carburated hydrogen, and the two combinations occupy a volume much more considerable than that of the vapour of water; so that the action of caloric is favourable to their production, independently of the concurrence of the affinities.

263. Oxygen, in the gaseous state, appears to have a greater quantity of caloric than every other substance, for there is not any known which suffers so much of it to escape by the changes of its constitution.

This property cannot be directly proved, for when the oxygen gas, by passing into any combination, abandons its caloric, the heat produced may be attributed to the substance with which it combines: but if it is considered that the substances in which the oxygen retains the greatest part of its caloric, such as nitric acid, oxygenated muriatic acid, and some oxides, all possess the property of giving out a great deal, when their oxygen passes into other combinations; if it is considered that those which occasion the disengagement of much caloric, give only a much smaller quantity, by forming other combinations, it cannot be doubted that the greater part of that which is set at liberty during combustion, must be attributed only to the change in the state of the oxygen.

Since many have been induced to attribute the disengagement of caloric only to the changes of dimensions of bodies, and particularly of the  
gases

gases which become fixed, it may be supposed that the hydrogen contributes much, if not the greatest part, of the heat produced by the formation of water; but, on the one hand, it is solid bodies, such as phosphorus, which occasion the greatest emission of caloric with a given quantity of oxygen gas; on the other hand, when water is decomposed by means of sulphuric acid and iron, much heat is excited, and, nevertheless, all the hydrogen of the water which is decomposed, resumes the elastic state: the heat, therefore, must proceed from the change in the state of the oxygen, and the caloric necessary to enable the hydrogen to pass into the gaseous state can only be a small part of that disengaged from the oxygen in its passage from the state in which it was in the water, to that which it takes by combining with the iron.

Although the oxygen holds a great proportion of caloric in combination, of which it abandons a greater or less quantity by changing its state, its specific caloric is nevertheless weak; for according to the experiments of Lavoisier and Laplace, its specific caloric is to that of water, only as 60 to 100, which proves more strongly that specific caloric has no known relation with absolute caloric (150).

Since oxygen and hydrogen not only combine in the gaseous state, but can also produce water when they are already in a state of combination, either in the same substance, or in two separate substances,

substances, the phenomena dependent on caloric, and principally on that which is disengaged from the oxygen, correspond with the state in which the oxygen is found in the combinations which it abandons to produce water with the hydrogen.

These extensive properties of oxygen were in a great measure unnoticed, before Lavoisier made known its combinations, and analysed the numerous phenomena which depend on it: it was a happy epocha for chemistry, when Black had just laid the foundation of the theory of heat; when Priestley, by new processes, discovered a great number of gaseous substances, till then neglected; when Cavendish united the application of a luminous physical knowledge with the most delicate researches of chemistry; when Bergman methodized all the processes which serve to direct chemical action, and to class the effects of it; when Guyton established a communication between all the opinions, and weighed them; when Fourcroy began to publish, with celebrity, the rapid discoveries to which he contributed. Suddenly the experiments of Lavoisier elucidated a great part of the phenomena which chemists had been obliged to leave unexplained, or of which they gave only an incomplete interpretation, by the medium of an ideal supposition on which they bestowed the importance of a reality, and obtained him the foremost rank among French chemists.

The combination of oxygen with the other substances is accompanied with different phenomena,



according to the quantity of caloric which is disengaged: when this quantity is very small, it is a simple oxygenation which takes place; when it is considerable, and produces much heat, and also light, it constitutes what is called combustion, and the body which undergoes it, is properly called combustible, or inflammable: these two species of combination differ therefore only in an indeterminate degree; it is nevertheless proper to distinguish them, by considering oxygenation as a more general phenomenon, and combustion or inflammation as belonging to a part of the oxygenable bodies, in the circumstances which are favourable to the action of the oxygen: oxygenation, considered in all its extent, comprehends the greatest part of chemical phenomena, of which it is the immediate cause, or to which it contributes more or less.

The two substances, laying aside the metals, phosphorus and sulphur, capable of producing the phenomena of combustion, which is only distinguishable from simple oxygenation by the great proportion of caloric disengaged, are hydrogen and carbon, which by their combination with oxygen form water and carbonic acid: it is to the hydrogen and the carbon that the other compound bodies owe the characteristic properties by which they are classed among inflammable or combustible substances.

It is therefore to the formation of water and carbonic acid that the phenomena of combustion are



are principally owing, whether it is accompanied by a great change of the temperature, or whether it produces less sensible effects, a slow and obscure combustion, and changes of constitution, which afterwards have their value in chemical action. A subject of such importance in the production of the phenomena with which chemistry is occupied, requires that the most correct possible idea should be formed of these two species of combination.

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## CHAP. II.

### *Of the reciprocal Action of Oxygen and Hydrogen: Of the Action of Water.*

265. WE may distinguish two descriptions of processes, by which the memorable operation of the composition of water has been performed, for the purpose of ascertaining all the results.

In the first, which has been employed by Lavoisier and Meusnier, and by all those who have since endeavoured to bring this to perfection, a globe is filled with oxygen gas, into which hydrogen gas is passed, and combustion is produced by means of electricity; an alternate afflux of

c 2

hydrogen

hydrogen gas and oxygen gas is made from reservoirs, called gazometers, whose immersion in water determines the quantity of the gas which they furnish, so that the combustion may be maintained by suitable proportions of each gas, until the gaseous residue of the combustion opposes its continuation: at this period, if it is desired to continue the operation, the gas is withdrawn by an air-pump, and the process is recommenced.\*

In the second process, Monge,† after having formed a vacuum in a globe, introduced a quantity of oxygen gas, which, at the temperature and pressure of the atmosphere, would have filled the twelfth part of its capacity, he then filled it with hydrogen gas: having interrupted the communication between the globe and the graduated cylinders which supplied the gases, he inflamed the mixture by electricity: he introduced a new twelfth of oxygen gas, and so on in succession: when the gaseous residue prevented the explosion, he withdrew it by means of an air-pump, and recommenced the introduction of the gases, and the successive explosions.

This process has the inconvenience of subjecting the vessels to being broke by the force of the explosion; but the graduated cylinders made use of by Monge to measure the quantities of the

\* Mém. de l'Acad. 1782.

† *Ibid.* 1783.

gases, have as much precision, and are much less expensive than the gazometers.

Water, more or less pure, and a gaseous residue is obtained in both processes; this residue is formed, 1st, of azote gas, which is always in greater or less proportion in the oxygen gas, according to the substances from which this has been obtained, and which are usually oxygenated muriate of pot-ash, which yields it in the greatest purity of any of them, oxide of manganese, and oxide of mercury: 2d, of carbonic acid gas, which is usually in greater or less proportion with the oxygen gas, when it has been obtained from oxide of mercury or oxide of manganese: the quantity of this acid is much diminished by washing the gas in lime water; but it cannot be entirely taken away by this means: a part also arises from the hydrogen gas, either because it was held in solution in it, or because it has been formed by the combustion of the carbon which the hydrogen gas always contains in greater or less quantity when it is obtained from iron, as it generally is; 3d, at the conclusion of the operation, there is found, with the carbonic acid and azote gas, more or less of oxygen gas and hydrogen gas, which have been unable to enter into combination, because of the mixture of the other gases, which obstructed the combustion.

To compare the results of the operation with the quantities of the gases made use of, the specific gravity of these gases, at a certain temperature,

ture, is ascertained, and the residue is analysed, which, with the water produced, must represent their weights.

266. The liquid which is produced is not always pure water, it frequently contains nitric acid, the quantity of which is found by means of pot-ash, which forms nitrate of pot-ash.

Cavendish, *who appears to have first noticed\* that the water produced in this combustion was the result of the combination of two aeriform fluids, and that its weight equalled theirs*; also first noticed the production of nitric acid in the formation of water†. According to his observations, this acid is formed when the oxygen gas made use of contains but a small proportion of azote gas; its quantity is increased when a certain quantity of azote gas is added to the oxygen, to the amount of one-fourth of its volume nearly; on the contrary, less acid is obtained when atmospheric air is used, more than three-fourths of which are azote gas; and, finally, the formation of nitric acid is avoided by employing so large a proportion of hydrogen gas that no oxygen gas remains free.

On the other hand, Fourcroy, Vauquelin, and Seguin have observed, that if the combustion is made very slowly, no nitric acid is produced; but that this combination takes place as soon as the combustion acquires a certain vivacity.

\* Rapport fait à l'Acad. par Lavoisier, Brisson, Meusnier et La Place, Recueil de Mém. par Seguin. Tom. II. p. 309.

† Philos. Trans. 1784.

In this case heat produces the same effect as the electricity in the experiment by which Cavendish formed nitric acid; but we have seen that the effects of electricity correspond with those of a temperature much more elevated than the action of light or the ebullition of water (135); so that it is only with a certain briskness of combustion that nitric acid can be produced.

In this production of an acid there is one circumstance which is probably deserving of attention: Keir having examined some water which Priestley had formed by the combustion of hydrogen gas, and which contained some acid and a little oxide of copper, says,\* that he kept the liquid in ebullition with distilled water and pure nitric acid for half an hour, to carry off all the nitrous gas which it might contain, and that nevertheless solution of silver precipitated muriatic acid from it; whence he concluded that the muriatic acid is produced with the nitric acid, as in several other operations of nature.

Cavendish had also observed, that the nitric acid he formed gave a small precipitate with solution of silver, but he attributed this precipitate to the nitrous state of the acid, and proved that nitrate of pot-ash, reduced to a nitrite, also produced a precipitate: I shall nevertheless remark, that nitric acid, strongly impregnated with nitrous gas, does not produce any precipitate with

\* Philos. Trans. 1788.



solution of silver, and that there is not any obtained by passing a great quantity of nitrous gas through a solution of silver: in this respect the solution of silver is not like that of gold, from which the gold may be precipitated in the metallic state by a nitrite, as was shown by Tennant.\*

By means of the preceding observations, the operation may be easily managed so as to obtain only pure water, and the formation of the nitric acid, and the circumstances which hinder or favour it, may be accounted for.

If the quantity of azote gas is very small, it is retained by the uncombined oxygen gas, and does not produce nitric acid; this can only be formed at a more elevated temperature than that necessary for the water; so that when the combustion is well managed, the water is pure, even when the oxygen gas employed contains a proportion of azote gas favourable to the production of this acid, and when it is similar to that of atmospheric air, only a very small quantity of this gas, or even none, can be obtained; because then the combustion has not much vivacity; finally, if, during the operation, the hydrogen gas is in sufficient proportion, no nitric acid is formed, because water is produced in preference, so that hydrogen gas would decompose nitric acid at a high temperature: it is obvious, therefore, that in Monge's experiment, in which the hydrogen

\* Philos. Trans. 1797.

gas was always predominant, no nitric acid could be found, although there was a sufficiently considerable quantity of azote gas: the water which he obtained also gave scarcely any signs of acidity.

To prevent the inaccuracies which might have arisen from water held in solution by the gases submitted to combination, Lavoisier and Meusnier caused these gases to pass through dried muriate of lime, with which the tubes that conducted them into the vessels wherein their combination was effected, were imperfectly filled; the quantity which they then contained was so extremely small, that it could not occasion any error in the results; nevertheless these results show that water is composed of 85 ponderable parts of oxygen, and of 15 of hydrogen nearly, a proportion which may be satisfactory in common circumstances; but according to the experiment made by Fourcroy, Vauquelin, and Seguin, with a precision which it is difficult to attain, the weights of oxygen and hydrogen which enter into the composition of water are in the following relation; oxygen, 85,662; hydrogen, 14,338: and the volumes of the gases employed in the combustion are, oxygen gas, 15,837; hydrogen gas, 32,517: so that the volume of oxygen gas is to that of hydrogen gas as 1 to 2,050.\*

267. No trace of the elementary affinities of oxygen and hydrogen can be perceived in water,



their saturation appears to be complete; nevertheless, as these two elements, in addition to their mutual affinity, have also one for other substances, so water has a resulting affinity which is powerful, though different from the distinctive affinity of the oxygen, and from that of the hydrogen. It does not affect the characteristic properties of other substances, while it does not experience decomposition; one part of its effects takes place in that space of the thermometric scale between the freezing and boiling points of water, and forms the hygrometric phenomena; but in some cases affinity unites another quantity of water with much more force, and we shall see that alumine can retain a tenth of its weight of it at the highest degree of heat: this affinity of the water, which modifies the reciprocal action of the molecularæ of a substance, or of the integrant parts of a combination, is the principal cause of the separations occasioned by a difference of solubility. I have given a good deal of attention to these effects in the first part of this work, I shall nevertheless again notice those which depend more immediately on the action of the water, and on its different states.

The action of water on solid substances weakens the effects of the reciprocal action of their molecularæ or of the integrant parts of their combinations, and when it becomes sufficiently powerful it reduces them into the liquid state; but solids produce an opposite action on it, and when  
this

this action is preponderant, they reduce it to the solid state : they accelerate the term of its congelation as it accelerates the term of their liquefaction by caloric.

The action of the solid bodies with which water combines, produces, therefore, the same effect on it as the reduction of temperature ; it reduces it to the solid state, with this difference, that when its *moleculæ* are only influenced by their mutual action, the phenomena of congelation take place in succession, so that those which pass to the solid state, take an arrangement, more or less symmetric, which augments the dimensions of the ice ; but when, for example, it is solidified in salts, it does not experience this accidental increase of volume, which is proved by the salts being condensed in crystallizing (142) : if the water took the dimensions of ice, they would, on the contrary, experience a dilatation on passing to the solid state, and a condensation by liquefaction.

When it takes the solid state in this manner, by the action of the integrant parts of salts, it may, in proportion to its quantity, communicate properties to them which depend on the reciprocal action of the solid *moleculæ* ; it serves as an intermedium to them, and may be said to be the cement which unites them to each other ; but it renders them more or less fusible by heat : it has no influence on the symmetrical arrangement when its quantity is small, but in a large quantity  
it

it is capable of varying the forms of the crystallization. (*Note XIV.*)

When it communicates liquidity, it may change the state of saturation of combinations by exercising a more powerful action on one of their elements; but it is only by this change that it contributes to the state of saturation which results from its action.

Water retains an action on the other gaseous substances; it can dissolve them more or less, and reduce their volume, though this reduction is generally very inferior to that which accompanies stronger combinations, as is proved by the facility with which they are restored to their elastic state.

The elastic effort which these substances, as well as the water itself, retain, in this state of solution, constitutes their tension, by which a part resumes the gaseous state whenever the pressure is removed, or when it is assisted by the affinity of the atmospheric air: it is augmented by heat, which favours the disengagement of the gaseous substance, as is also done by opposing a fixed base to the action by which it is retained more strongly in a combination: but the tension varies according to the proportions of the water, as we have seen that it varied in ether by the action of alcohol (*Note XVII.*); and what I have said on the comparative tension of alcohol and ammonia (165), is only applicable to these substances, as well as to muriatic acid and to all the liquids arising

ing from the combination of a gas with water, or with any other liquid, by supposing them to be in a uniform state.

From the different comparisons which I have shown, it will be seen that water acts by an affinity similar to that of all those substances which do not occasion any change in the properties of others, by altering the state of their saturation; but as soon as it begins to be decomposed it produces this effect, and then gives birth to combinations which have peculiar properties, and of these, the principal shall be examined in succession.

Oxygen which is held in solution by water enters easily into combination with other substances; thus the oxide of iron precipitated from green sulphate\*, passes to a more advanced stage of oxidation in water; phosphorated azote becomes luminous, and a portion of nitrous gas passes to the state of acid: only part of this air is driven off by ebullition, for phosphorated azote also becomes luminous with distilled water, and with that which has been boiled.

To decompose water, a more powerful action is required, such as a strong electric shock, which at the same time drives off the oxygen gas and the azote that might be held in solution, even by distilled water†; but it is generally by the concur-

\* Scheele, de l'Air et du Feu.

† Tennant. Philos. Trans. 1797.

rence of several forces that this decomposition, which confirms the results of the composition in the most satisfactory manner, is effected.

268. Iron is generally employed for this purpose: at a common temperature it scarcely produces the decomposition of the water; but at a more elevated temperature, when the force of cohesion of its parts is very much weakened, this decomposition is effected with much more facility: the metal does not receive all the quantity of oxygen with which it could combine in atmospheric air, but takes only a little more than a fourth of its weight; so that, at this degree of oxidation, the action it exercises on the oxygen is insufficient to effect any further decomposition of the water.

Even in this circumstance, it appears that it is only from the concurrence of the expansive action of caloric on the hydrogen gas, that the decomposition can be effected, since, by avoiding this action, the hydrogen gas, in its turn, can decompose all the oxide of iron (261).

The concurrence of the action of an acid which tends to combine with a metal in the state of oxide, favours the decomposition of water, so that then the metal which alone could not have caused it, is enabled to produce this effect, as is observed in the solution of copper in muriatic acid, which, alone, is incapable of decomposing water.

This decomposition of water, by means of which a metal is dissolved in an acid, and which throws the greatest light on many chemical phenomena,

was



was foreseen by La Place, as soon as the composition of this liquid was established by direct experiments: he concluded that this effect took place, because the acid employed for the solution was not decomposed, and because the oxygen which became fixed with the metal could only be owing to the decomposition of the water\* ; and this conclusion soon became a very fertile and generally received truth.

The water produced by the combustion of hydrogen gas requires only a much smaller quantity of caloric to maintain it at the same equilibrium of temperature as the gases from which it is obtained, the pressure being the same ; the power of combination of the caloric has consequently been diminished by that established between the oxygen and hydrogen ; the quantity which has become superfluous is partly disengaged under the form of light and radiant heat ; the remainder raises the water to a much more elevated temperature than that of the gases which formed it, and it receives a much greater expansion : the heat which reduces it into vapours gives it a volume which is nearly in the proportion of 1600 to 1 of that of the liquid. On considering the specific gravity of the oxygen gas, and that of the hydrogen gas, which produced the water, it will be seen that the volume of the water which is formed would be much less than that of the two gases, at the same temperature, if at the instant of its production it was only at the degree of ebullition, but it is at a much higher temperature ; whence it follows that it takes dimensions

\* Mém. de l'Acad. 1781.



much larger than those of the gases were which form it: from this it arises that when the combination of oxygen with hydrogen is made with too great quantities of the gases, the vessel is burst with violence.

This force, acquired by the vapour of water, is not to be considered as an increase of elasticity, since it is only occasioned by the change of temperature; if it is brought to the same thermometric degree as that of the oxygen and hydrogen gases before their combination, it can only form vapour, which has not only a specific gravity nearly double that of the mixture of the gases, but which can only resist a feeble pressure; it then passes to the liquid state, and when the temperature approaches that of congelation the reciprocal action of the *moleculæ* gives birth to the force of cohesion.

The effect of the caloric disengaged in the combustion of hydrogen gas has been compared with the heat necessary to melt ice\*: it was observed that one ponderable part of hydrogen gas, by its combination with a proportional quantity of oxygen, liquefied rather more than 300 parts of ice, so that the caloric disengaged in the production of one part of water, is sufficient to melt nearly 50 parts of ice, or to raise 50 parts of water from the degree of congelation to 75° of the centigrade thermometer; which would give for the temperature of the vapour of water, at the moment of its formation, 3750 degrees equal to those of the thermometric scale, above the point at which the gases

\* *Mém. recueillis par Seguin, tom. I.*

were in the moment of their combination, if one part of the caloric was not employed in reducing the water into vapour, and did not become latent in consequence of the dilatation produced by it; and if another part of it did not escape in light and radiant heat.

Since the gaseous state is not necessary to enable the oxygen and hydrogen to form a combination, and as they can also produce water when they are already in a state of combination, either in the same substance, or in two separate substances, the phenomena which depend on the caloric, and principally on that abandoned by the oxygen, correspond to the state of the oxygen in the combinations which it abandons to produce water with the hydrogen (264).

269. The processes in which the action of water is employed, and the explanation of the phenomena which depend on it, require therefore that a distinction should be made in those arising from the affinity by which it unites to substances without experiencing any change in its state of saturation, or occasioning any in that of the substances; those which depend on the changes of saturation made in a combination, because it unites with one of its elements rather than with another (216); and, finally, those in which its elements experience and produce a change of combination and saturation.

The changes of state which it undergoes from the differences of temperature, or from the action

of other substances, must also be distinguished: it may pass into an elastic state or a solid state by either means.

Finally, it absorbs or it abandons caloric according to the changes it experiences; and the elements which form it eliminate more or less, in their combination, according to the quantity of it which they contained, so as to retain only that which is suitable to the state in which it is found.

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### CHAP. III.

#### *Of Charcoal and Carbonic Acid.*

270. CHARCOAL owes its predominant character to its strong affinity for oxygen, but it has also a powerful one for hydrogen, and it is the mutual affinities of these three elements which complicate both the combinations resulting from them, and the effects which are peculiar to them: this also renders it difficult to class the facts which exhibit the composition of charcoal, the distinctive properties which it gives to the combinations it forms, and the phenomena dependent on the action of its elements: in this chapter I shall principally consider the composition and properties of charcoal, and those of the carbonic acid which it produces by

by its combination with oxygen; and in the next, those of the gases which owe their distinctive properties to carbon and hydrogen: but some of the subjects treated of in one chapter may not receive the necessary elucidations until the following one.

Charcoal is not a simple substance: hence it arises that the element which predominates in its composition, and to which it owes its distinctive properties, and particularly its fixity, which resists the most powerful action of caloric, when it is not obliged to give way to the formation of some combination, has been distinguished by the name of carbon.

By its combination with oxygen, the charcoal gives rise to carbonic acid: Lavoisier, to whom this important discovery is owing\*, made several experiments to determine the proportions of carbon and oxygen which form carbonic acid, but he did not succeed, as he confesses himself, in attaining the precision he wished: the results of some of his experiments gave 28 ponderable parts of carbon and 72 of oxygen, and others gave 24 of carbon to 76 of oxygen.

This determination would be of great importance, not only in judging of the products of combustion, but in discovering the composition of a great number of substances in which the charcoal is associated with hydrogen, and in estimating the properties dependent on each, as well as the diffe-

\* Mém. de l'Acad. 1781.

rent combinations which may be produced by a change in the forces which maintained them.

271. In the experiments which he made on the combustion of charcoal, Lavoisier discovered that it contained the hydrogen which formed the water during the production of carbonic acid: by the weight of this water he estimated the proportion of hydrogen which it held, in one experiment, at  $\frac{1}{8}$  of the weight of charcoal: but not having perceived any water when he employed calcined charcoal, he considered it as deprived of hydrogen in this state.

Nevertheless Kirwan observed that charcoal which he had kept for a long time at a red-heat, produced a great quantity of sulphurated hydrogen gas mixed with a little hydrogen gas, when he urged it by fire in a retort, with a mixture of sulphur\*.

As a different result has been lately given†, I repeated the experiment with charcoal strongly calcined at a forge fire the instant preceding: by employing 30 grammes of the charcoal with 20 grammes of sulphur in an earthenware retort, I obtained more than 100 cubic centimeters of sulphurated hydrogen gas, which was ascertained to be such by its inflammation and by its solution in water which produced the usual effects with metallic salts. The disengagement of this gas only ceased because the sulphur was entirely sublimed,

\* Philos. Trans. 1785.

† Ann. de Chim. No. 125.



and there can be no doubt that, if sulphur had been added to the charcoal which remained in the retort, more sulphurated hydrogen would have been obtained.

If the calcined charcoal had not given sulphurated hydrogen, no conclusion could be drawn from thence against the existence of the hydrogen, because by its proportion being too much diminished, it might be retained by a force so powerful that the sulphur, whose volatility would occasion its speedy separation, might not be able to disengage any more: but since, notwithstanding this circumstance, it had been obtained from charcoal strongly calcined, and by a heat much lower than that which it had before supported, and since there can be no doubt of the existence of hydrogen in the sulphurated hydrogen, this fact is a positive proof that the charcoal itself, after having been submitted to a strong calcination, contains the hydrogen.

Those who were present at the experiments which Lavoisier made on the combustion of strongly calcined charcoal may recollect that water was always deposited on the sides of the vessel, which formed streaks, and even ran in little streams at the commencement of the combustion; but at the end of it this water was entirely dissolved.

The first effect of the combustion of charcoal is easily ascertained by an experiment, for which we are indebted to Hassenfratz\*; it is only re-

\* Mém. de l'Institut. Tom. IV.



quired to pass oxygen gas through a red-hot tube in which strongly calcined charcoal is placed; at the commencement of the operation it will be seen that a considerable quantity of water is deposited at the extremity of the tube, and the gas disengaged forms a cloud in the jar into which it is received; so that it also deposits water on cooling.

Cruikshank noticed that when a mixture of a metallic oxide and charcoal strongly calcined is urged by the fire, a little water is always disengaged\*; and he concluded from this observation, and from some others, that calcined charcoal always contains a little hydrogen.

272. If strongly calcined charcoal contains hydrogen, it follows that, in its combustion, all the oxygen which is employed does not serve for the production of carbonic acid, but that a part must combine with the hydrogen to form water; nevertheless if charcoal strongly calcined is employed, no water is perceptibly deposited, as was observed by Lavoisier: whence it may be concluded that carbonic acid retains a quantity of water which is not manifested when it is formed by the combustion of charcoal. Is not this quantity that which produces hygrometric phenomena?

We have seen (172) that, at the same temperature, and at the same degree of humidity, the gases all contain the same quantity of water, which, in its state of solution, takes the dimen-

\* Observ. addit. 19 Avût. 1801. Bibl. Britan.

sions of a permanent gas, and which produces the hygrometric phenomena; but this quantity is too small to explain the phenomena which have just been mentioned, and those which will presently be noticed, for 100 cubic centimeters, at a temperature of  $15^{\circ}$ , can only contain a little more than a milligramme.

Instead of the hygrometric water, either of the oxygen gas or of the gas which is disengaged at the commencement of a slow combustion, being capable of giving the explanation of the water which is deposited, the hygrometric property of the gas disengaged, and which is proportional to the high temperature in which it is found, must disguise a considerable part of that which is formed, so that the quantity of hydrogen which was contained in strongly calcined charcoal necessarily exceeds that which enters into the water deposited in the circumstances described; and nevertheless it is only a little of the charcoal which contributes to it. When therefore charcoal, strongly calcined, produces carbonic acid by a combustion in which no water is perceived, it must be combined with the carbonic acid in a state different from that which is in simple solution, and which produces the hygrometric phenomena.

I have endeavoured to determine the quantity of the water which can be disguised in the formation of carbonic acid, by inquiring into the proportions which could best agree with the specific gravity of some hidro-carbonated gases, the quantities

tities of oxygen gas which was necessary to their combustion, and those of the carbonic acid arising from it; but the results which I obtained can only be considered as uncertain approximations, because a supposition, remote from that which I employed, would have given a difference of composition which corresponds equally with the specific gravity: nevertheless I shall make use of these results in the following chapter, because they are adapted to show the relations of the composition of the different gases which I then examined; but they must only be considered as hypothetical to a certain point.

I shall confine myself to concluding, in this place, that the most strongly calcined charcoal contains the hydrogen which, with the oxygen, produces a quantity of water that may be rendered sensible; that this water may become latent in the ordinary formation of carbonic acid; and, that it exceeds that which, retained by a weak affinity, preserves the dimensions suitable to its gaseous state, and produces hygrometric phenomena.

273. Charcoal can form combinations without its molecule ceasing to exercise the mutual action to which it is indebted for its force of cohesion: from this cause these combinations have much less stability than those in which the reciprocal affinity exercises all its power.

Fontana, Priestley, Scheele, and Morozzo, proved that charcoal has the property of absorbing  
different

different species of gases, and particularly carbonic acid: Rouppe and Noorden have repeated and varied these experiments; from the Memoir published by the first,\* it results that charcoal cooled without the contact of air possesses this property, which is also greater in proportion as the temperature is lower; that the part of the atmospheric air which is not absorbed retains its eudiometric state; that the temperature of boiling water is sufficient to drive off the absorbed gas; and that charcoal impregnated with hydrogen gas forms water, even with the production of heat, when it takes oxygen gas.

From these observations, it may be concluded that when charcoal is fresh prepared, it will absorb atmospheric air and carbonic acid, whence may arise the small quantity of carbonic acid, of azote gas, and of water, which, when it is submitted to distillation, passes at the commencement; but no oxygen gas is obtained, which should have been the case, if the observation of Rouppe, who is of opinion that, by an elevation of temperature, the absorbed gases are disengaged in their integrity, is admitted without restriction.

274. Carbonic acid, which can only be formed when the temperature has diminished the resistance of the force of cohesion of the charcoal, has an acid power which is very considerable, and which even appears to be superior to that of the sulphuric

\* Ann. de Chim. Tom. XXXII.

acid, since the carbonate of lime, and that of barites, have a much greater proportion of earthy base, than the sulphates of lime and of barites: I have observed, that in this view, an exact comparison of the carbonic acid with the others cannot be made, because the carbonates made use of had frequently an excess of alkalinity (87); it is not known whether the carbonates with earthy bases, have also this excess, but this consideration only adds to the idea which must be formed of the power of the carbonic acid.

It is not therefore surprising that carbonic acid adheres with such force to fixed bases, when the salts which it forms do not contain water, which, by its affinity for it, favours its disengagement, and serves as an intermedium between it and the base which retains it.

Withering observed that the native carbonate of barites could not be decomposed by heat alone, while the artificial carbonate could\*: he attributed this to the water of which the first was deprived, and by means of which the second abandons its carbonic acid; but nitric acid sufficiently weakened, which can supply the requisite water, disengages the carbonic acid from the first as well as from the latter.

Priestley confirmed the opinion of Withering, by disengaging the carbonic acid gas of the native carbonate of barites by means of the vapour of

\* Philos. Trans. 1784.



water, which he caused to pass over this carbonate, placed in a tube upon red-hot coals\*. He endeavoured to estimate the quantity of water which united with the carbonic acid, and he concluded, from his experiments, that it was equal to half the weight of the acid; but this estimation is doubtless much exaggerated: it even appears to me that the species of experiment which it requires is not susceptible of a degree of precision which can be depended upon; the barites which has abandoned the carbonic acid will retain part of the water, for it manifests a great affinity for it; the carbonic acid must be received into a vessel of a large capacity, on whose sides a quantity of water may be deposited which it is difficult to estimate, and which greatly alters the results; a small difference in the temperature varies the quantity of water which remains in solution in the carbonic acid, and which affects its volume.

Pelletier was equally unable to withdraw the carbonic acid by exposing the native carbonate of Siberia to the action of heat, and he was obliged to employ acids very much diluted to obtain the solution†.

The greatest part of the other acids, and even acetic acid much concentrated, are unable to dissolve the native carbonate, unless a certain quantity of water is added to them.

\* Philos. Trans. 1788.

† Ann. de Chim. Tom. X.



Are we not warranted in concluding that this constant difference between the native and artificial carbonates, whether in the action of heat or in that of the acids, and which is made to disappear by the simple addition of water to the first, is owing to the water which is retained in much greater quantity in the last?

But the artificial carbonate itself only yields part of its carbonic acid by the action of heat, as was observed by Chenevix\*, and it is probable that its decomposition would have been effected by employing Priestley's method.

I have admitted too easily (173), on the authority of Clement and Desorme†, that the action of air may supply that of water, by causing a current of it to pass over the native carbonate of barites; experience has undeceived me: I passed a current of air, in the manner they direct, over the native carbonate placed in a porcelain tube, exposed to a strong heat; the air in its passage through the lime-water really indicated a small quantity of carbonic acid, but, having broken the tube, I observed that the fragments of the carbonate were only alkalised where they touched the tube, and that those parts had contracted a yellowish grey colour, and seemed to have promoted the fusion of the surface; but all those parts which

\* Bibl. Britan. Tom. XVIII.

† Ann. de Chim. Tom. XLIII,

had been most exposed to the action of the air remained in a perfectly neutral state.

Afterwards I urged some pieces of the carbonate by a strong fire, in a covered crucible, and they became sensibly alkaline without the assistance of water, and without any current of air.

It is not therefore strictly correct to say that the native carbonate of barites does not experience a decomposition by the sole action of heat; it can be alkalisied to a certain point; I should, however, premise that although the carbonate I employed was very transparent, it contained a little sulphate of barites, so that the alkalisied part occasioned a black precipitate in solution of lead: nevertheless it dissolved in nitric acid without a residue.

Although this sulphate may have had some influence, the experiment I have inserted proves that the current of air opposes instead of favouring the decomposition of the carbonate; and that it only causes the small quantity of carbonic acid, which without it would have remained in the interior of the tube, or which would have been insensibly absorbed at the surface of the water, to become perceptible: and this effect has nothing in common with that arising from the vapour of the water in Priestley's experiment.

The effect, which is attributed to the slight solubility of nitrate of barites, in explaining the inaction of the acid on the native carbonate, when a certain quantity of water is not added to it, should

should also take place with the artificial carbonate which nevertheless does not require this addition of water: the muriatic and acetic acids, which form more soluble salts, should act without the addition of water, and nevertheless all the acids show the same difference between the native and artificial carbonates.

275. The carbonate of barites is not the only one whose carbonic acid refuses to yield to the action of heat, either wholly or in part. Carbonate of pot-ash itself, according to the observation of Pelletier, only gives out a small part of its carbonic acid by the action of heat, and it must be remarked that even when the native carbonate of barites retains all its carbonic acid, it attacks the crucible, and reduces it into glass, as was observed by Klaproth; this also happens with carbonate of pot-ash, so that glasses are then obtained which contain much carbonic acid.

Kirwan says\* that Black was never able to calcine carbonate of lime in any considerable quantity in an argillaceous crucible, without vitrifying it, and that he could only accomplish it in a black-lead crucible, whose influence we shall see; and that Smith met with the same difficulty. Pictet also has endeavoured to decompose carbonate of lime, but in vain; he could only obtain a small quantity of carbonic acid from it, without the assistance of water. From these observations

\* Bibl. Brit. Tom. XV.

it is probable that it is only by means of the vapour of water formed by the combustion, or which is disengaged from the combustible substances, that the lime-stone is converted into lime in the kilns where this operation is performed; nevertheless chemists know that marble can be completely reduced into lime, and this difference seems to arise from the water which the marble retained during the crystallization of its particles.

Finally, if it is considered that lime and magnesia do not combine with carbonic acid, unless water is added, we are warranted in supposing that carbonic acid requires a certain proportion of water to enable it to pass into solid combinations; and that when this proportion is diminished to a certain degree, it cannot be driven from the combinations which it has formed, unless the greatest part of it is restored, or the nature of it is changed by the methods which will be discussed in the following chapter.

It is obvious, therefore, that water intervenes by its affinity in the greatest number of cases in which carbonic acid is disengaged, when it is itself held by a weaker affinity; it then retains a greater faculty of acquiring the elastic state, and seconds a similar tendency in the carbonic acid, as ether accelerates the vaporisation of alcohol, and water that of sulphuric acid.

It may at first appear difficult to admit the existence of water in substances which are exposed to

to the strongest fires ; but is it more difficult to conceive than that of the carbonic acid, which is possessed of a much greater disposition to elasticity, and which, notwithstanding, enters into glasses not decomposable by the highest degrees of heat, as we have just seen ? Does not alumine retain water at the highest possible degree of heat ? We may therefore admit the supposition of this water, if, besides the considerations I have just offered, we attend to those phenomena which cannot receive any plausible explanation but by means of the existence of water in carbonic acid, or in its combinations.

276. It must not, however, be concluded that carbonic acid cannot exist in the gaseous state without the concurrence of water ; this may be one of the differences between the carbonic acid formed by the combustion of the diamond, and that which arises from the combustion of charcoal : thus as the properties of the diamond, and the differences discovered between it and charcoal, seem to prove that it is composed of carbon, which does not retain hydrogen in combination, the carbonic acid formed by its combustion cannot contain water, and consequently, with an equality of base, must have less specific gravity ; so that by comparing it with the carbonic acid which has been enabled to saturate itself with water, such as it is obtained in the greatest number of circumstances, errors will be occasioned in its valuation ; and  
although



although this subject has employed some skilful chemists, I am of opinion that it requires new investigations.

It is this want of hydrogen which renders the diamond much less combustible than charcoal, or which occasions it to require a much more elevated temperature, although it may have been subjected to a great mechanical division: the carburet of iron or plumbago seems, in this respect, to hold a medium between charcoal and it; for, although in Kirwan's experiments it did not give sulphurated hydrogen by treating it with sulphur, other considerations nevertheless prove that it does contain hydrogen, and, in particular, its property of favouring the decomposition of the carbonates, like charcoal.

Guyton, who has established the chemical character of the diamond by many experiments, has proved that it also possesses the property of converting iron into steel. Mushet has raised some doubts on this interesting experiment; he pretended that iron might be changed into steel in vessels closed with care; so that, according to him, no conclusion can be drawn from the conversion of iron into steel: but Mackenzie has proved\*, by experiments made with great care, that the iron preserved all its characteristic properties, when it was exposed to the greatest heat in closed vessels, without any mixture which could change it, even

\* Journ. de Van. Mons. No. 2.

although the vessels were so cracked as to permit the introduction of gaseous substances: he also confirmed the reduction of iron into steel by the diamond.

277. The combustion of one part of charcoal in the calorimeter, liquefied 96 parts of ice; which gives, for one ponderable part of carbonic acid, nearly 24 parts of ice liquefied, or 24 parts of water raised from the temperature of congelation to 75 degrees of the centigrade thermometer, or, an equal weight of water to 1800 degrees of the same thermometer.

But to determine the quantity of caloric arising from the combination of the carbon with the oxygen, it is necessary to deduct from this quantity that which arises from the water produced (267), and which is principally in a state of combination. The carbonic acid which is formed, is raised to a more elevated temperature than the water, in the inverse ratio of their capacity, or of their specific caloric.

In the combustion of those substances which are used as the common aliment of fire, a quantity of caloric is disengaged proportionate to the quantities of water and carbonic acid which can be formed, according to the composition of these substances: this caloric in part takes the form of light, or of radiant heat, which, in furnaces, enters speedily into combination, or which is reflected by the fire-places according to the inclinations of the surfaces; but the greatest part remains combined

bined with the water and carbonic acid which it has raised to a high temperature, until this temperature can be shared with the neighbouring bodies ; so that more heat is obtained in proportion as the gaseous substances which are formed are subjected to a greater circulation in which they can part with it.

Azote gas forms more than three-fourths of atmospheric air : at the first instant, it divides the heat with the water and the carbonic acid, in proportion to its capacity for heat and to its quantity, and it exhales with them : this occasions the water and carbonic acid to be suddenly reduced to a much lower temperature than they would have been if they had not been united with the azote.

If the proportion of atmospheric air is too great, the superfluous part makes a useless division of the heat which is disengaged, and carries it off in its exhalation, so that the temperature is much less raised : if the current of air is not rapid, the caloric is communicated proportionally to the neighbouring bodies, and the temperature is but little raised near the fire-place : the height of the passages for the gas which has experienced combustion determines the rapidity of the current, by the vacuum which is formed by the reduction of the vapours which exhale.

From these properties combined with the greater or less conducting faculty of the bodies which should either maintain or communicate the temperature produced by the combustion of a suitable

proportion of the combustible substance and atmospheric air, are deduced the conditions most advantageous in obtaining the greatest effect of combustibles: conditions which have been determined with the greatest attention by a celebrated philanthropist, in the principal uses in society.

Oxygen gas, by its combustion, produces a much brisker heat than atmospheric air, because the azote gas does not divide it with its combinations: its disengagement is also much more rapid, and this also increases its effect; because, the communication of heat requiring a certain space of time, it must accumulate faster when the combustion is brisk than when it is effected slowly.

This property of oxygen gas has been employed to produce degrees of heat which cannot be attained with atmospheric air in the most skilfully constructed furnaces, and which can scarcely be obtained from the strongest lenses and the largest concave mirrors.

Many chemists have employed themselves with the processes best adapted to draw the greatest advantage from this powerful means of increasing the heat, and applying it, either by directing the jet of oxygen gas on the substance submitted to experiment, and which is placed on charcoal, or by causing the oxygen gas to meet with hydrogen gas: Lavoisier, in particular, Ehrman\*, and lat-

\* Essai d'un art. de fusion, etc. par Ehrman; suivi des mém. de Lavoisier.

terly, Robert Hare\*, have improved these processes, and multiplied the experiments.

278. Charcoal, therefore, is not a simple substance, but is indebted to carbon for its distinctive properties, and principally for its fixity: without losing its force of cohesion it can form with different gases, which it reduces to its state, a combination which does not sustain an elevation of temperature equal to that of the ebullition of water; nevertheless the oxygen which is absorbed in this manner seems to remain fixed in it, until it can enter into a more intimate combination: but at every known temperature charcoal retains hydrogen whose effects must be estimated in the combinations which it forms.

The principal combinations of charcoal which take the elastic state are carbonic acid, and the compound inflammable gases which we are about to examine.

The quantity of caloric eliminated by the oxygen gas in the formation of carbonic acid, is determined by that which is required for the new combination. Carbonic acid contains carbon and oxygen in a proportion to which only approximations have yet been obtained, because the hydrogen of the charcoal produces at the same time a certain quantity of water which becomes latent.

This water retained by the powerful affinity of the carbonic acid, must not be confounded with

\* Mem. on the supply and the application of the blow-pipe.

that



that which produces hygrometric effects, and which only experiences an action incapable of changing the dimensions which are suitable to it in the state of elastic vapour (168). This water is manifested by the methods which can decompose it.

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## CHAP. IV.

### *Of Carburated Hydrogen, and of Oxi-carburated Hydrogen.*

279. WE have seen that charcoal is composed of carbon and hydrogen, and that, in the experiments of Lavoisier, the common charcoal must have contained  $\frac{1}{8}$  of its weight of hydrogen, to which is to be added the undetermined quantity which it retains after the most powerful calcination, and which was neglected by Lavoisier.

Charcoal strongly calcined may be considered as a uniform combination with the exception of the small quantity of ashes and of salts which may be found, in proportions a little different, but which do not contribute to the properties it possesses as an inflammable substance: this is not the case with charcoal which has not been submitted to a strong heat; it may contain a greater or less proportion of hydrogen, according to the circumstances

stances of the operation by which it was prepared, and perhaps according to the composition of the wood from which it was made. It is probable that the properties which are distinguishable in its use may arise in a great measure from this; we shall also notice another difference.

Nevertheless there is a limitation in the quantity of hydrogen which charcoal can retain, as well as in all the combinations of gaseous substances with those which are fixed, and which must overcome the resistance of the elasticity. Beyond this term, there is an interval between the proportions which compose the charcoal whose distinctive properties are owing to the carbon, and those of the gaseous combination formed between the carbon and the hydrogen, and in which the properties of the hydrogen become predominant, and more particularly by the state of elastic fluid which is owing to it. This elastic fluid is the carburated hydrogen gas.

Until very lately the inflammable gas which contains only carbon and hydrogen, and another species of inflammable gas which, at the same time, contains oxygen, and which I have thought it right to designate by the name of oxi-carburated hydrogen, have been confounded under the same denomination.

The theory which I have embraced on this subject is in opposition to that supported by Guyton and his pupils, who consider the gas which I call oxi-carburated as differing only from the composition

sition of carbonic acid, by having a larger proportion of carbon, thus excluding the hydrogen.

The opinion of the celebrated chemist with whom I maintain this discussion, is of such weight that I could not but fear I had been in some error: this has induced me to enter into details, by which a judgment may be formed of the reasons on which my theory is founded: besides this point, which at the first blush, appears to be only a slight difference, of little interest, becomes important to the complete knowledge of the phenomena of combustion, of the reduction of metals, and of the results of the analysis of vegetable and animal substances, and is connected with the most general principles of the science.

When such of the oxides as retain the oxygen with a strong affinity are reduced by means of charcoal, neither water nor carbonic acid are obtained, nevertheless the oxygen has entered into combination, and the metal is reduced: the theory which supposes only two combinations of the oxygen with carbon and hydrogen, namely, carbonic acid and water, has nothing to oppose to the objections Priestley drew from these facts, which he was the first who noticed. Woodhouse multiplied the facts, but did not undertake to develop the cause\*; which Cruikshank executed with success†. Before his experiments were known to the

\* Ann. de Chim. Tom. XXXVIII. et XXXIX. Mém. de l'Institut. Tom. IV.

† Bibl. Brit. Tom. XVII. et XVIII.

French chemists, they had been employed in analogous inquiries; and the discussion, of which I have spoken, was commenced between them. As, however, those of Cruikshank have the priority of date, and were, in general, made with much care, I shall principally derive the results from them.

280. The analysis of the compound inflammable gases is founded on the property which hydrogen gas and carbon have, of forming combinations with oxygen in determinate and known proportions, and which it is easy to distinguish; so that by these combinations we can determine the quantity of the two inflammable elements which enter into the composition of a gas whose specific gravity must be known: if these two elements, by their union, give this specific gravity, it is a carburated hydrogen which has been examined, and in which no other ponderable element could exist: if, on the contrary, they can only form part of the weight, we must suppose there is some other ponderable substance to complete it; and this can only be such a proportion of hydrogen and oxygen, that it enters into the composition of the water: the necessary quantity of hydrogen and oxygen is added to obtain the specific gravity of the gas which is then oxi-carburated.

This kind of analysis is capable of great precision in the carburated hydrogen gases, when their specific gravity has been accurately determined: for there does not remain any uncertainty,  
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except on the proportion of the oxygen which enters into the composition of the carbonic acid, in attributing that which is suitable to the formation of the water whose proportions are well known; but as the weight of the hydrogen is only about a sixth of that of the water, a small difference in the method of estimating it, is reduced to a small quantity in the determination of the composition of the gas. That of the elements of the oxi-carburated gases is subject to a greater uncertainty; the quantity of hydrogen which enters into their composition being much less, a small difference in the adopted bases may lead to a great one with respect to the proportion of the hydrogen, or even render its existence doubtful.

Besides, the latter gas being less combustible, a part of it easily escapes from the combustion, principally by the action of the carbonic acid, which is also capable of disguising its inflammability: it appears, likewise, to receive a certain portion of azote into its composition, which, without doubt, is variable in the different species, and which has hitherto been neglected. The objects of the analysis must, therefore, be limited to ascertaining the considerable differences which are found in the composition of this species of gas, and to drawing those consequences from it which are applicable to the explanation of the phenomena offered in the reduction of the metallic oxides, and the decomposition of carbonic acid, and of other oxygenated substances, which left an ob-  
scurity



scurity in this part of the theory that no one had attempted to dissipate before Cruickshank, but hitherto no great precision has been acquired with respect to the proportions of the elements which compose it.

I have observed, that to obtain the most complete combustion of oxi-carburated hydrogen gas, it is necessary to cause it to detonate with a great excess of oxygen gas, so that I employ one part of the first with at least two parts of the latter, although only a portion of it is required for the combination; another precaution not less necessary is, to wash the oxi-carburated gas with lime-water, for I have found that simple water left a tenth of its volume of carbonic acid, and it is to these circumstances that I attribute the differences found between the results which have been published and mine. There was a greater consumption of oxygen gas, and more carbonic acid produced in my experiments, although, on repeating them several times, they gave but very small differences.

281. The carburated hydrogen gas, therefore, requires more oxygen gas for its combustion; it burns with a red or white flame according to its vivacity.

The quantity of oxygen gas which combines, compared to that of the carbonic acid which it forms, and to that of the water whose production must be supposed to complete its combustion, indicates a quantity of carbon and hydrogen which  
is

is represented by its specific gravity, and the water which is deposited proves its production.

Different species of it may be distinguished which vary in their origin, in the proportions of their elements, and in their state of dilatation: I shall particularise them, taking 100 cubic inches, or 1989.45 cubic centimeters of each, and neglecting the differences which may arise from the variations of temperature and pressure.

1st. The gas obtained by distilling four parts of sulphuric acid and one of alcohol, and which was made known by the Dutch chemists\*: the properties which they discovered in it, caused them to give it the name of olefiant gas: its specific gravity, combined with the products of the detonation, show that it contains nearly 1.560 grains of carbon, and 0.520 of hydrogen. It may be considered as the carburated hydrogen gas which contains the greatest proportions of its two elements.

If this gas is driven through a red-hot tube, it forms a carbonaceous deposit and a little black oil in it, and a carbonaceous smoke passes into the receiver, but no carbonic acid: in this operation it experiences a very small dilatation in its volume, and it is then composed of only 0.572 of carbon, and 0.312 of hydrogen, so that it has acquired a great specific lightness, although the proportions of the carbon and hydrogen of which it is composed are but little different from those of the preceding.

\* Journ. de Phys. An. 2.

2d. The gas arising from alcohol which is passed through a red-hot tube : according to the Dutch chemists who have described it, its specific gravity is 0.436, that of atmospheric air being 1.000 : experiment shows that it contains 0.780 of carbon, and 0.260 of hydrogen, which also corresponds with its specific gravity.

3d. The gas obtained when an oil is distilled : there is a little difference in this gas according to the period of the operation ; that disengaged at the commencement has a little more hydrogen and a little less carbon than that which is yielded near the end : the first is composed of 1.144 grains of carbon, and of 0.260 of hydrogen ; and although its specific gravity has not been determined, the great similarity it has with the olefiant gas leads me to conclude that it does not contain other principles.

4th. The gas proceeding from the decomposition of water by charcoal, which contains nearly 0.260 grains of carbon, and 0.208 of hydrogen ; this is very little different from the specific gravity determined by Lavoisier and Meusnier.

According to the experiments of Cruikshank, that which is obtained from camphor, and from the distillation of animal substances, may be included among the carburated hydrogen gases.

282. The following are the principal differences which distinguish the oxi-carburated hydrogen gas from the preceding : it is much less combustible ; it requires a much less quantity of oxygen ;

it

it burns with a blue flame, although this property is not to be considered as constant and distinctive; it yields much less water during its combustion, and sometimes it does not yield any apparently; it has generally a greater specific gravity, nevertheless this is not, as was thought by Cruikshank, a character by which it can be distinguished, for that of the olefiant gas is generally as great; besides it is variable in this respect.

Both gases are decomposed by oxygenated muriatic acid, but with some differences; it appears from the experiments of Cruikshank that the carburated hydrogen gas, on being slowly decomposed by the action of oxygenated muriatic acid, is, in part, converted into oxi-carburated gas; but this may also be decomposed by the oxygenated muriatic acid, as is proved by the experiments of Guyton and Cruikshank: nevertheless the latter noticed that the electric spark did not inflame the mixture of oxygenated muriatic gas, and of oxi-carburated hydrogen gas, as it does with the carburated hydrogen gas, so that he gives this as a method of distinguishing the two gases: it appears, therefore, that the oxygenated muriatic acid decomposes the carburated hydrogen gas more easily than the oxi-carburated, which is conformable to the opinion that might be formed from their respective compositions.

The oxi-carburated gas is formed in different circumstances, the principal of which must be examined,

examined, by determining which of them cause its production, and which, on the contrary, give birth to other combinations, with a view to the attainment of a general principle as a guide in the explanation of the phenomena which depend on them.

1st. If four measures of olefiant gas are detonated with three of oxygen gas, instead of a condensation of volume, a dilatation is observed; the seven measures occupy the space of eleven, and a carbonaceous deposit is formed on the eudiometer: on submitting this new gas to detonation with a suitable proportion of oxygen, its analysis shows that it is composed of carbon, in a quantity corresponding to that of the primitive gas, taking into the account the small portion which formed the carbonaceous deposit; of its hydrogen, with the exception of a very small part which produced the water; and of the oxygen employed in the first detonation, *minus* the small quantity which has entered into the composition of the water.

The carburated hydrogen produced by the distillation of an oil, and in which the carbon is in much greater proportion, also experienced a dilatation by detonating four parts of it with three of oxygen gas; but with the olefiant gas a little water was formed, while in this case, a little carbonic acid was produced: the analysis of the dilated gas also shows that it is composed of oxygen, hydrogen and carbon: Cruikshank observed this dilatation before me, and described nearly the same effects.

These



These two experiments prove demonstratively the existence of a species of inflammable gas which is composed of oxygen, carbon, and hydrogen, and which is a true oxi-carburated hydrogen; so that the existence of this species of gas is no longer hypothetical.

In the second place, they show that this gas may receive very different proportions of its three elements; for the analysis of the first dilated gas differs considerably from that of the second. In this respect, therefore, the oxi-carburated hydrogen resembles the carburated, which admits very variable proportions of hydrogen and carbon into its composition.

This experiment also evinces that it is peculiar to oxygen gas to increase the dimensions of a gaseous combination into which it enters, unless this effect is attributed to the small diminution of the carbon; but the opponents of my opinion reserve this expansive property for the carbon, and deprive the oxygen gas of it, contrary to every indication of the properties of these substances, one of which has naturally the greatest fixity, and the other a considerable disposition to the elastic state.

I must not conceal that a result contrary to the experiment I have just analysed has been published: it is said\*, *when carbonated hydrogen is inflamed in Volta's eudiometer, if there is not a suffi-*

\* Journ. de l'Ecole Polytech. XI<sup>e</sup> Cahier.

*ciency of oxygen for the total combustion, the charcoal alone burns, the hydrogen resumes its elasticity, which its combination with the charcoal had caused it to lose, and the volume of the gases is dilated : it is then a mixture of carbonic acid and hydrogen, which burns blue like the carbonous gas, but which, after washing with lime-water, is diminished and leaves a residue of pure hydrogen.*

I shall not offer the simple testimony of the experiments, the details of which I have published, but Cruikshank has observed, as well as me, that the dilated gases, obtained by the methods pointed out, gave a quantity of carbonic acid corresponding to that of the carbon which it still retained in a great proportion, although he did not draw the necessary consequence from it, that this gas is analogous to that which he called *gaseous oxide of carbon*.

In every known circumstance, it is the hydrogen, particularly when it is in a considerable proportion, which first undergoes combustion, unless it forms a triple combination : Cruikshank precipitated charcoal from the olefiant gas by the oxygenated muriatic gas, which also produced the combustion, of the hydrogen more easily than that of the charcoal : it is thus that the sulphurated hydrogen gas and also the phosphorated, abandon part of the sulphur and the phosphorus in an incomplete combustion, or by the action of an insufficient quantity of oxygenated muriatic acid.

The authors of the Memoir which I have quoted

themselves relate an experiment whose result is diametrically opposite to the first, without any reason for this difference being perceptible in the circumstances : they passed an equal quantity of hydrogen gas and of their carbonous gas through a red-hot tube, and assert that the latter deposited its charcoal on the interior of the tube : it is true Theodore de Saussure has shown that they were deceived in this respect\*.

283. 2d. When common charcoal is submitted to distillation, at the commencement only a little carbonic acid and a small quantity of water are disengaged ; after this a great quantity of inflammable gas is obtained, of which, the first portions give much more carbonic acid, by detonations with oxygen gas, than those which follow, and which form the greatest part of the whole quantity. This latter gas does not give more than a tenth of its volume of carbonic acid ; by the products of its detonation it is found that 100 cubic inches (1981.45 cubic centimeters) contain 0.104 gr. of carbon and 0.208 of hydrogen, which is not equivalent to its specific gravity : here then is a gas in which a proportion of oxygen and hydrogen proper to form water must be admitted, that the results of its analysis may correspond with its specific gravity.

I make use in this place of numbers determined by experiments which I have repeated with care, but I do not mean to be understood that there are

\* Journ. de Phys. Brum. An. XI.

no differences in this respect in different charcoals, or that circumstances, difficult to appreciate, may not cause a variation in the results.

Common charcoal is doubtless composed of carbon and hydrogen, since nearly a fourth of its weight of an inflammable gas is obtained from it, in which the properties of the hydrogen predominate; this hydrogen cannot proceed from the water, for whenever water is decomposed, a proportionate quantity of carbonic acid is formed; now only a very small quantity of carbonic acid is obtained from the distillation of charcoal, which is disengaged at the commencement of the operation: it cannot be supposed that the oxygen of the decomposed water is retained by the charcoal, for considering the great quantity of hydrogen which predominates in the disengaged gas, and the great proportion of oxygen which enters into the composition of water, charcoal, urged by a strong fire, could be scarcely any thing but condensed oxygen; it must at least have properties which would be very different from those of common charcoal, whereas there is only a difference which is naturally accounted for by a smaller proportion of hydrogen: besides, we have seen that the existence of hydrogen in charcoal, strongly calcined, is capable of direct proof.

Charcoal not calcined, on the contrary, contains a certain proportion of oxygen which enters into the formation of the oxi-carburated hydrogen obtained from it, and it appears to me natural to

attribute the separation of the hydrogen to its affinity for oxygen, so that when the oxygen is exhausted in the charcoal, or at least when only a very small quantity remains, the heat ceases to disengage the inflammable gas, and in this respect the charcoals will be found to differ from each other.

In the actual state of our knowledge, it cannot be decided whether the small quantity of water and of carbonic acid disengaged at the commencement of the distillation are a new production, or whether they existed in the charcoal, because this has the property of condensing a certain quantity of all the gases (273).

Cruikshank attributed to the inflammable gas obtained from charcoal, a specific gravity nearly equal to half that of atmospheric air: it is obvious, from the quantity of carbonic acid which he obtained from its combustion, and which amounted to more than 40 parts in 100, that it was that obtained at the commencement of the distillation which he experimented upon: he thence concluded that it was a carburated hydrogen gas; but it is easy to be satisfied that the quantity of carbon indicated by that of the carbonic acid, and the proportion of hydrogen necessary to saturate the oxygen gas which he employed, are not sufficient to occasion the specific gravity of this gas, and that nearly the half of its weight must be sought for in some foreign substance, which is necessarily a proportion of oxygen and hydrogen capable of forming water,



water, so that it results from his own analysis that this gas must be placed among the oxi-carburated hydrogens.

Here then is another inflammable gas, in which, in my opinion, the existence of hydrogen and oxygen with carbon cannot be denied.

284. 3d. Oxi-carburated hydrogen gas is produced when the carbonic acid which is retained in a combination is decomposed on urging it by a strong fire with charcoal, also strongly calcined, or when a metallic oxide, or a sulphate, or finally any substance which only yields its oxygen at a high temperature, is treated in the same manner.

The carbonate of barites which is capable of resisting the action of heat, is decomposed when it is exposed to the action of fire in a plumbago crucible, as was observed by Hope; Pelletier produced this decomposition by the mixture of a little charcoal: he ascertained that instead of carbonic acid, it was oxi-carburated hydrogen gas that was disengaged.

A carbonate treated with a very oxidable metal also produces oxi-carburated hydrogen.

Carbonic acid which is kept in contact with red-hot charcoal is also changed into oxi-carburated hydrogen gas.

Such are the principal facts on which the two opinions under discussion are formed.

It is asserted that the inflammable gas which I call oxi-carburated differs from carbonic acid only by a greater proportion of carbon; I am of opinion

opinion that it receives hydrogen into its composition, that it is indebted to this element for its specific lightness, which was ascertained by Cruikshank, and by Clement and Desorme, to be greater than that of atmospheric air; that this hydrogen may arise from the charcoal, which contains it even when it has been strongly calcined; from the water which some substances can retain at the highest degree of heat; and very often from both.

Before discussing these opinions, I shall repeat that a great number of chemical phenomena may receive two or more explanations which may seem to fulfil all the conditions, and then it will be impossible to decide in favour of either, until some fact arises which will only admit of one of these explanations, or which cannot be reconciled with the general principles founded on the comparison of a great number of phenomena, which, having been carefully analysed, cannot be controverted, except by means of this explanation.

Thus when the decomposition of water by some of the metals is examined alone, the disengagement of hydrogen gas may be equally explained, either by supposing that the hydrogen existed in the metal, and that its place is supplied by the water, or that the water experiences a decomposition: this double explanation continues if the oxide is reduced by hydrogen gas: but if the attention is directed to the fixation of oxygen in an oxide, such as that of mercury, and on its reduction,

duction, in which the oxygen abandons it by the sole effect of an elevation of temperature; if the elements which are combined in the formation of water, and the results obtained from its decomposition are compared; if, at the same time, the correspondence of the hydrogen gas disengaged during the oxidation of a metal by water, with the weight acquired by the metallic oxide are examined, there is no longer any doubt; a choice will be made between the two hypotheses.

It is the same with the decomposition of metallic oxides, carbonic acid, and other substances, which, when they are decomposed with the assistance of the action of charcoal and of heat, give birth to an inflammable gas. If the attention is only directed to the material results of this decomposition they may frequently be accounted for by a simple combination of a large proportion of carbon, or by the introduction of hydrogen into the combination of carbon and oxygen; but if the principles which are most firmly established are applied to the results obtained in the first supposition, there will be found such a disagreement, that, in my opinion, no difficulty can remain as to the choice which should be made.

285. In all the experiments by which Cruikshank decomposed the gas in question by oxygen, with a view to ascertaining its composition, he obtained water, one only excepted: he even determined that the proportion of hydrogen was to that of carbon as 1 to 7. Thus, his results are perfectly

perfectly analogous to mine, except in a single experiment which I shall explain. He also ascertained that charcoal strongly calcined contained hydrogen. There is therefore only this difference between his opinion and mine, that from his object being the overthrow of Priestley's doctrine, he did not think it necessary to take the hydrogen into the explanation of the properties of the gas he had discovered, although he admitted its existence in it, and that he took the name of the gas only from its two other component parts: for my own part, I do not attach much importance to this difference of nomenclature.

In the experiment in which Cavendish did not get water by detonating the gas he obtained, and which alone can occasion any difficulty, because it is single in experiments of this description, that is to say, those in which the gas furnishes a great quantity of carbonic acid, which does not permit the effective appearance of water, I am of opinion that the water which really forms, is not apparent, because its quantity is only equal to what can be held in solution in the carbonic acid, and this opinion is founded on all the reasons by which I think I have proved that charcoal strongly calcined contains hydrogen, and that this hydrogen produces the water, which is rendered latent in the carbonic acid.

By this single modification in the opinion of Cruikshank, the gas which does not give water by its combustion is assimilated to all the other  
gases



gases of this species, in which his experiments likewise prove the existence of hydrogen, and no other difference is perceptible between them but what may be attributed to the smaller proportion of hydrogen.

286. Let us inquire what are the consequences of the composition of the inflammable gas, when the hydrogen is entirely excluded from it, and when its formation and properties are accounted for by the sole difference in the proportions of the charcoal and the oxygen.

From the analysis of this gas it is concluded that it is formed of 53 ponderable parts of charcoal, and 47 of oxygen, and in this hypothesis the charcoal must be considered as being absolutely deprived of hydrogen. We may observe in the first place that the charcoal is very fixed, and consequently shows but little disposition to take the elastic state.

To avoid all the influence of hydrogen, it is stated that carbonic acid is composed of exactly 28 ponderable parts of carbon and 72 of oxygen: whence it follows that 100 parts of oxygen gas combined with 39 parts of carbon yield carbonic acid, whose specific gravity is nearly one-third greater than that of oxygen; that in this state it can form another combination, in which the 100 parts of oxygen are united to 112 parts of charcoal; that consequently the carbonic acid is enabled, by means of heat, to overcome the resistance it must encounter from the fixity peculiar to



to 73 parts of the charcoal. The oxygen gas which, by its conversion into carbonic acid, had taken a specific gravity proportionate to the quantity of carbon combined with it, acquires, from its combination with nearly twice as much of the fixed substance, a specific lightness which is not only greater than that of carbonic acid, but also than that of oxygen gas.

Thus the carbon combines, in the first instance, with the oxygen gas, without sensibly changing its dimensions, by those peculiar to itself, when it is not retained in the solid state by the reciprocal action of its molecu<sup>læ</sup>; a much greater specific gravity is the result, and thus far the general character of combinations is preserved; a double quantity of carbon is now added to this combination, and it not only destroys the first effect, that is to say, the increase of the specific gravity, but it gives it a specific lightness greater than that of the oxygen gas.

It has been said that the caloric might produce this dilatation so contrary to every idea which can be formed from every combination known; let us therefore examine this effect, with regard to the action of the caloric: in the combination of 39 parts of carbon with 100 of oxygen, a great quantity of caloric is eliminated, and allows a greater condensation in the parts of the gaseous fluid; it must afterwards exercise an action entirely opposite to the first; it must give the gaseous state to 73 parts of carbon, which resists  
its

its action completely when it is insulated, and besides this, it must exercise so powerful an action on the combination, that its *moleculæ* are kept at a greater respective distance than even those of the lightest of its two elements: the first result of the irregular action attributed to the caloric would be diametrically opposite to that which it would produce in the continuation of the same combination, and in the same condition of temperature: the force which produces combination, and which is universally acknowledged to be an attraction, tending to approximate the particles which undergo the combination, in this case would be changed into repulsion.

The difficulties resulting from the comparison of the specific gravities would become also more irreconcilable, if Desormes and Clement had established the calculation of the parts which compose the oxi-carburated hydrogen gas, by accurate experiments; for 100 measures of that which they employed constantly gives from 96 to 100 measures, by its combustion, while they say they only obtained about 80.

They would be further increased if the dilatations which the carburated hydrogen gas experiences from the action of the electric spark, were taken into the consideration. (*Note XX.*)

287. 4th. In the direct combustion of charcoal, effects are observed which correspond exactly with those I have just discussed, according to the proportion of oxygen which can combine with the carbon,

carbon, and according to the circumstances which can occasion the introduction of hydrogen into the combination, so that, they are capable, by their correspondence, of elucidating the explanation of each other.

If common charcoal is burnt in a sufficient quantity of oxygen gas, water and carbonic acid are formed; if the charcoal has been strongly calcined, the water is only perceived at the commencement of the combustion, but it disappears, it is dissolved in the carbonic acid in the course of the operation: it considerably exceeds the quantity which produces hygrometric phenomena, but it is also incapable of contributing to them, since, supposing the oxygen gas to be saturated with humidity, the carbonic acid gas which results from it, and which nearly equals its volume, could not abandon the hygrometric water until it was reduced to a temperature inferior to that which the oxygen gas had possessed (172).

When the quantity of oxygen gas is only received by successive portions, as when it is passed over strongly calcined charcoal in a red-hot tube, according to the experiment of Hassenfratz which I have quoted, the phenomena vary according to the temperature, yet the production of water is always perceived at the commencement of the operation, notwithstanding the elevation of temperature which should cause it to disappear: this water cannot arise from the charcoal, because it had before experienced a degree of heat incomparably

parably more considerable ; it must therefore have been formed by the combination of oxygen with that part of the hydrogen which was least strongly retained by the charcoal, and is an incontestable proof of the existence of hydrogen in charcoal strongly calcined.

After this, if the temperature is a little raised, much carbonic acid is formed, and a little oxi-carburated hydrogen gas : it is obvious, that at this period of the operation, the charcoal yields carbon with more facility ; but if the heat is stronger very little carbonic acid, and much oxi-carburated hydrogen are, on the contrary, obtained : how can the temperature cause this difference ? It appears to me that it is a natural effect of the action by which heat augments the elastic disposition of the hydrogen which is retained in the charcoal, and whose existence can no longer be disputed, so that by the concurrence of heat with the affinity of the oxygen, the hydrogen quits the charcoal or enters with it into a gaseous combination ; if there is too little oxygen to produce the water and the carbonic acid, oxi-carburated hydrogen is principally produced ; a ternary combination is formed instead of two binary ones.

The reduction of the oxides by charcoal offers similar phenomena ; for, as was justly observed by Cruikshank, those of the oxides which can be reduced with facility, and consequently at a temperature but little raised, form much carbonic acid ; on the contrary, those which require an elevated



elevated temperature, yield only oxi-carburated hydrogen, or very little carbonic acid, and when the two gases are produced in certain proportions, the greatest quantity of carbonic acid is obtained at the commencement of the operation, and towards the end the proportion of oxi-carburated hydrogen increases, as has been already shown by Woodhouse.

Carbonic acid may be changed into oxi-carburated hydrogen gas, either by the action of charcoal when a carbonate is treated with charcoal, or by causing the carbonic acid to pass through red-hot charcoal ; it experiences a similar change if at an elevated heat it is placed in contact with a metal which has the property of decomposing water; but there is one difference in the result. In the first case, according to the observation of Clement and Desormes, it acquires a volume more than double ; but if iron is employed, it appears from the experiments of Cruikshank, that no dilatation is produced : in the one case, the hydrogen of the charcoal, and the water contained in the carbonic acid seem to concur in the production of the oxi-carburated hydrogen gas ; in the other, the water which was retained by the carbonate contributes alone to the change which is effected, by yielding its oxygen to the metal and its hydrogen to the carbonic acid, which also yields part of its oxygen to the metal.

If either carburated hydrogen or oxi-carburated hydrogen is detonated with a sufficient proportion  
of



of oxygen gas, two combinations, whose elements are in the state of the greatest condensation, are formed, water and carbonic acid, which are insulated and separated by means of the properties which belong to the state they have acquired ; but if there is not a sufficient quantity of oxygen to produce these two combinations, the mutual affinity existing between the carbon, the hydrogen, and the oxygen, retains them in a single combination, in which the obstacle they reciprocally oppose prevents them from experiencing so great a contraction as in the water and carbonic acid.

288. Such is the general principle from which may be deduced the various phenomena which have been observed in the decomposition of carbonic acid, of the sulphates, and of the oxides, by charcoal, and in the formation and decomposition of oxi-carburated hydrogen : *In every case in which the proportion of oxygen is too small to produce water and carbonic acid, with the carbon and hydrogen, a ternary combination is established, which is the oxi-carburated hydrogen, the proportions of whose elements may vary according to the circumstances in which it is formed.*

*If the carbonic acid, or any other oxygenated substance is readily formed, the same circumstances which would have given rise immediately to oxi-carburated hydrogen, produce it by means of these combinations ; but it is reduced into water and carbonic acid, when it can acquire a sufficient proportion of oxygen.*

The

The conditions necessary to the formation of oxi-carburated hydrogen will often occur in combustion. In fact, when charcoal is urged by fire in a furnace, and the current of air is not very considerable, a great quantity of gas is disengaged which burns by the contact of atmospheric air, and yields a flame whose blue colour proves that it is oxi-carburated gas. This blue flame is often seen in the combustion of wood when it is not brisk; in fine, when the stream from a blow-pipe is directed on the flame of a lamp or candle, the impelled air begins by forming oxi-carburated hydrogen, which afterwards burns of a blue colour; and from this arise the reductive effects obtained by plunging the body experimented on into the interior flame, that is to say, into the oxi-carburated gas, and the contrary effects of the oxidation produced by the exterior flame, by means of the high temperature, and the free contact of the air.

Carbon and hydrogen can therefore form two species of combination, one in which the carbon predominates, and which is fixed, and the other in which the hydrogen is superior, to which it then owes its gaseous state.

Oxygen can produce a ternary combination with these two first elements; it is found in charcoal, but only in a small proportion; it can form a gaseous combination and enter into it in a much larger proportion; this is the oxi-carburated hydrogen gas, and although the hydrogen can only exist in it in a small quantity, it is the most efficacious

efficacious cause of its elastic state, and of its specific lightness.

I am of opinion that the existence of this gas is proved, principally ; 1st, because a similar one can be composed by combining a certain proportion of oxygen with carburated hydrogen gas, and, because that obtained from urging charcoal by fire is also of this species.

2d. Because the most powerfully calcined charcoal contains hydrogen, and no effect of this element is to be found so energetic, if it is not admitted that it passes into the oxi-carburated hydrogen gas which is formed by its means.

3d. Because the specific lightness of oxi-carburated hydrogen gas cannot be reconciled with the supposition that it is only composed of carbon and oxygen, and which requires that the oxygen, after having experienced a contraction in the formation of the carbonic acid, shall follow a course, so opposite, that the combination resulting from a much more considerable addition of a solid and scarcely expansive element, will become specifically lighter than that of its elements, which are naturally very light, and have a great disposition to elasticity, while the accession of hydrogen gives a natural explanation of this lightness.

Thus, this supposition is contrary to every thing which observation teaches us with respect to the other gaseous combinations, in which there is not any one known which acquires less specific gravity than the lightest of its elements : it is

subversive of the general principles which are the result of all the chemical facts, since it supposes that the combination is not owing to an attraction but a repulsion ; for we cannot here suspect a similar cause to that which dilates the volume of ice, although the constant effect of cold is to produce the approximation of the molecules ; in that case the arrangement assumed by the solid molecules may apparently destroy the effect of the real condensation they experience.

This ternary combination corresponds to that which in the solid state composes most vegetable substances, and when these are urged by the fire it takes the gaseous state, with a change of proportions.

It is analogous to the composition of the Prussic acid which results from the combination of azote, carbon, and hydrogen, and particularly to that of the other ternary acids, which are also owing to oxygen, hydrogen, and carbon.

If I have admitted different species of carburated gases, and oxi-carburated gases, it is only to distinguish those which are produced in similar circumstances ; for each of these species seems capable of being composed of all the intermediate proportions between the extremes in which the limits of these combinations are comprised.

## CHAP. V.

*Of the combinations of Sulphur and Phosphorus with Hidrogen and Carbon, and of the mutual Combinations of these Substances.*

289. LIKE charcoal, sulphur has a disposition to combine with oxygen and hydrogen, and although its affinity for oxygen is predominant, that which it has for hydrogen is also so powerful that their combinations give rise to many phenomena, even when they only act by a resulting affinity.

The combinations of sulphur with hydrogen have a great correspondence with those of carbon and hydrogen, which we have just examined; they have a still greater with those of phosphorus: but these bases themselves may combine.

Kirwan\*, and the Dutch chemists†, who have made many interesting experiments in sulphurated hydrogen, were unable to form sulphurated hydrogen gas, either by melting sulphur in a vessel containing hydrogen gas, or by passing the latter through a tube containing sulphur in a state of liquefaction: nevertheless Gengembre succeeded in producing phosphurated hydrogen gas, which has much analogy with it, by directing the focus of

\* Philos. Trans. 1785.

† Journ. de Phys. Tom. XI.



alens on phosphorus placed in hydrogen gas; which seems to prove that by directing heat in that manner on such substances, different effects may be obtained, as is observed in the reduction of metallic oxides by hydrogen gas (*Note XIX.*); but according to the Dutch chemists, carbonated hydrogen gas may produce sulphurated hydrogen. It appears that in their experiment the charcoal was abandoned by the hydrogen, for the sulphur took a black colour; nevertheless it should be repeated with care to determine the nature of the gas which is formed; it is not probable that it is sulphurated hydrogen alone, for the properties of charcoal announce that it has a much stronger affinity with hydrogen than sulphur has, but it may be a gas whose composition is yet unknown.

Sulphurated hydrogen is formed in many other circumstances: in some, heat causes condensed hydrogen to take the elastic state at the same time with the sulphur; in others, an affinity which tends to deprive the hydrogen of the substance with which it was combined, concurs with that of the sulphur.

It is formed in the first manner when sulphur is urged by fire with charcoal, sugar, oil, and other substances containing hydrogen, which combines immediately with it.

Sulphurated hydrogen is produced in the second mode, on decomposing water by the action of an acid on a metallic sulphuret: it is also obtained by urging the hidro-sulphurets and hydrogenated

generated sulphurets, in which it was previously formed by the decomposition of the water, by fire, or by decomposing them by an acid which does not easily yield its oxygen, as is the case with concentrated nitric acid, which decomposes the sulphurated hydrogen, instead of disengaging it.

We are indebted to Gengembre, not only for the knowledge of the composition of sulphurated hydrogen, and that of phosphurated hydrogen which he discovered\*, but also for the correct explanation of its formation, when it is owing to the decomposition of water; he has shown that while its hydrogen forms a gaseous combination with the sulphur or phosphorus, a corresponding quantity of sulphuric or phosphoric acid is produced which enters into combination with part of the alkaline base: it is by this means that the hydrogenated sulphurets, which we shall presently examine, are formed.

There is therefore this difference between the disengagement of sulphurated hydrogen by means of a metallic sulphuret, or by the decomposition of a hidro-sulphuret, or an hydrogenated sulphuret, that, in the first case, the sulphurated hydrogen is disengaged as it is produced, and that, in the second, it was formed, and held in combination before taking the elastic state.

Sulphurated hydrogen gas has a specific gravity which, according to Kirwan, is to that of air, as

\* *Mém. des Savants étrangers. Tom. X.* A second Memoir is unpublished.

10.000 to 9.038: Thenard found that 100 parts contained 70.857 of sulphur, and 29.143 of hydrogen\*; but these valuations suppose that the gas always has the same composition.

290. Sulphurated hydrogen reddens the tincture of turnsole; it combines with the alkaline bases, and forms hidro-sulphurets with them, some of which are capable of crystallizing: I have only noticed† the crystallization of hidro-sulphuret of barites; Vauquelin has described‡ that of the hidro-sulphuret of soda, and it is probable that others will be observed. Sulphurated hydrogen therefore possesses the properties of the acids; I am not, however, certain if its power is sufficiently energetic to produce the neutral state with the alkaline bases.

Sulphureous acid gas combined with water is not changed by contact of oxygen gas or atmospheric air, it only dissolves in them in the ratio of their comparative quantity. Sulphurated hydrogen gas is also not decomposed by oxygen gas, which only dissolves it and divides it with the water, as we have just seen in the sulphureous acid.

This is not the case when this gas is combined in a hidro-sulphuret: then it does not oppose the resistance of its elasticity to the oxygen gas, and in the state of condensation in which it is found it acts on it in a greater mass, in the same

\* Ann. de Chim. Tom. XXXII.

† Ibid. Tom. XXV.

‡ Ibid. Tom. XXII.

way as takes place with the oxygen in nitric acid, and in oxygenated muriatic acid; the action of its base is added to its own, as in the sulphites; it therefore changes into sulphureous acid; but as the hydrogen combines much more readily with the oxygen than the sulphur, there is, in this first change, a difference from the manner in which the sulphites pass to the state of sulphates: the decomposition begins with the hydrogen, and the hidro-sulphuret, which was at first without colour, takes a yellow tinge, and becomes a hydrogenated sulphuret: if the hidro-sulphuret had been prepared with great care, no sulphur is deposited when it is decomposed by an acid, the sulphurated hydrogen only exhales from it; but when it has become yellow by the contact of air, and has begun to take the character of an hydrogenated sulphuret, the liquid is rendered turbid by an indecomposable acid, and a deposition of sulphur takes place; which proves that in reality the hydrogen which held the sulphur in solution had partly entered into combination with the oxygen before the sulphureous acid was formed.

When an hidro-sulphuret or an hydrogenated sulphuret diluted with much water has been left some time exposed to the air, an indecomposable acid also causes it to emit vapours of sulphureous acid, and experiment proves that no sulphuric acid is formed; this arises from the same cause as that which influences the sulphur, at a temperature not sufficiently elevated, to yield only sulphureous

phureous acid, but no sulphuric acid : this limitation of the action of sulphur must include all the circumstances in which it enters into combination with oxygen, with but little energy.

If the oxygen passes from a combination in which it was strongly concentrated, so that it need not experience a new condensation to form sulphuric acid, or that it can act with a considerable mass, it causes the sulphur to pass immediately to the state of sulphuric acid : thus when sulphur is acidified by nitric acid, sulphuric acid is immediately formed ; when it is decomposed by a nitrate, it is also sulphuric acid which is produced, both for this reason, and because the caloric which is disengaged produces a high temperature.

It has been seen that the oxygen of the atmosphere begins by combining with the hydrogen of an hidro-sulphuret ; this combination is likewise much quicker and much easier when the oxygen itself is in a state of condensation ; it can, in that case, decompose the sulphurated hydrogen though it be not condensed ; hence it arises that the sulphureous acid decomposes sulphurated hydrogen ; the sulphur of the sulphureous acid, and that of the sulphurated hydrogen are precipitated in this decomposition, nevertheless the action of the water which holds the two gases in solution prevents the mutual decomposition from being complete : nitric acid and nitrous gas, for the same reason, decompose sulphurated hydrogen :  
the



the oxigenated muriatic acid shows the successive formation of water and sulphuric acid by the combination of hidrogen and sulphur; for when poured in a small quantity into a solution of sulphurated hidrogen, or of an hidrogenated sulphuret, it at first precipitates sulphur; but when it is used in a sufficient quantity, it immediately converts all the sulphurated hidrogen into water and sulphuric acid.

The action of sulphureous acid on sulphurated hidrogen, in the decomposition of an hidrosulphuret, or an hidrogenated sulphuret, offers a circumstance worthy of being noticed: when one of these combinations has been left some time exposed to the air, an acid renders it turbid immediately, but the vapours of sulphureous acid gas are not disengaged from it until after some moments, because while any sulphurated hidrogen exists, the sulphureous acid which is set at liberty, and which is in contact with it, is itself decomposed and destroyed, so that only what remains superabundant can exhale.

Sulphurated hidrogen, therefore, by its combination with an alkaline base, acquires the property of subduing oxygen gas, but it passes into the state of sulphureous acid: if the oxygen itself is condensed, it forms sulphuric acid immediately.

No combination of sulphur and charcoal is yet known: when sulphur is treated with charcoal, even strongly calcined, it takes a portion of its hidrogen from it, and forms sulphurated hidrogen.

Lampadius,

Lampadius\*, by the distillation of sulphur and charcoal by a strong fire, obtained a *liquid having the odour of sulphurated hydrogen gas, very inflammable, heavier than water, and which continued to retain its liquid state under water at 12—0 of Deluc. Exposure for some minutes to the free air is sufficient to convert this liquid into true sulphur.*

This description clearly indicates hydrogenated sulphur; nevertheless Clement and Desormes formed a combination which seems to have had much resemblance to the preceding, but which, from their description, could not be an hydrogenated sulphur: it appears to have contained charcoal in its composition, and although it was very volatile and very inflammable, they deny the existence of hydrogen in it. This substance requires new inquiries.

291. Phosphorus does not appear to combine with hydrogen gas at a low temperature, or rather it does not enter into combination in a proportion sufficiently great to produce combustion by the simple contact of oxygen gas; but at a more elevated temperature it dissolves in greater quantity; nevertheless this solution is only made in a variable manner. It has not been attempted to produce phosphurated hydrogen by means of charcoal and the oils; but Fourcroy says† that ammonia is

\* Journ. de Pharmacie, No. 8.

† Syst. des. Conn. Chim. Tom. II. p. 238.

decomposed, at a high temperature, by passing the gas over phosphorus in a porcelain tube, and that a mixture of hydrogen and phosphurated azote was thus obtained: on the other hand, Pelletier relates\*, that having passed ammonia into melted phosphorus, there was not any decomposition, but that a combination of ammonia and phosphorus was formed: it is probable that he took the two gaseous substances observed by Fourcroy for an ammoniacal combination; but it may be possible that these two gases can form a peculiar ternary combination.

It is by means of the action which the alkalis exercise on phosphorus, and by that of the decomposition of the water which it effects, that phosphurated hydrogen gas is produced, in proportion to the phosphate which is formed at the same time: Gengembre attributes to phosphurated hydrogen gas a specific gravity nearly double that of oxygen gas; but it is still less uniform in its composition than sulphurated hydrogen.

He had before observed that this gas is partly soluble in water; Kirwan made the same observation†. I concluded from my own experiments‡, that a tenth of its volume is dissolved, whether it is left standing over water, or its absorption is hastened by agitation; that while this solution is proceeding, phosphorus precipitates, and that the

\* Mém. de Pelletier, Tom. I.

† Philos. Trans. 1785.

‡ Ann. de Chim. Tom. XXV.

remainder of the gas had lost the property of inflaming at the temperature of the atmosphere ; but Raimond is of opinion\* that it is entirely dissolved in water deprived of air ; that it requires a little more than four parts of water to dissolve one of gas ; that this solution is decomposed by contact of air, and that a small quantity of phosphorus precipitates, which, without doubt, is a little oxidized ; but that it remains unchanged when it does not experience the action of air.

Gengembre remarked that phosphurated hydrogen gas was only partly inflammable by the simple contact of air, when formed without the assistance of heat : Kirwan also observed that sulphurated hydrogen gas was only partly soluble in water ; and that it differed in this respect, according to the process, and particularly according to the temperature employed : Chaptal, the son, ascertained the influence of heat on the properties of both gases, at the moment of their production, and he proved that by treating phosphorus with an alkaline solution, at a degree of heat sufficiently elevated, a phosphurated hydrogen gas was obtained, inflammable at a low temperature ; that with a less degree of heat the gas was not inflammable, except at a much more elevated temperature, and that either species might be produced at pleasure by varying the degree of heat : he also observed that the sulphurated hydrogen gas obtained at a

\* Ann. de Chim. Tom. XXXV,

low temperature was only partly soluble in water ; but when produced by a higher temperature it dissolved in a much greater quantity, so that a greater proportion of sulphur gives the sulphurated hydrogen more solubility in water, and phosphurated hydrogen, from the same cause, becomes more inflammable, and probably more soluble in water.

Sulphur does not seem to decompose water, even at a high temperature, unless by the assistance of other affinities : phosphorus placed in water, at a low temperature, decomposes it, but this decomposition only takes place by means of the double combination which is formed : on the one side the water is charged with phosphurated hydrogen, and then possesses all the properties of that which has been impregnated with this gas ; on the other the phosphorus combines with the oxygen of the water, whence it arises that its surface whitens, and when the water is saturated with phosphurated hydrogen, to a certain point, the decomposition stops ; but the oxidation may proceed further by the aid of light.

292. Sulphur and phosphorus combine together in different proportions, as was shown by Pelletier : one character of these combinations is to be much more disposed to liquidity than the component substances ; that formed of equal parts of the two substances remains liquid to  $4^{\circ}$  Reaum.\* ; so that the mutual action of the two substances is

\* Mém. de Pelletier, Tom. I.



more efficacious by the diminution of their force of cohesion, than by the condensation they must themselves take (205).

When the combination of sulphur and phosphorus is formed without water, it swells if it is thrown into that liquid, and bubbles are disengaged from it which are luminous in the dark, and which often even inflame spontaneously, and with explosion in the air.

From this easy combustibility it is evident that it is phosphurated hydrogen gas which is produced, and that consequently it is the phosphorus which decomposes the water. The sulphur, by procuring it this liquidity, favours the action, as do all the solvents which destroy the effects of the solidity: in this case, while one portion of the phosphorus forms phosphurated hydrogen, another must oxidate, or become acid.

If the combination of sulphur and charcoal is still doubtful, this is not the case with that of phosphorus: with charcoal it yields, as has been shown by Proust\*, a red combination from which the phosphorus cannot be driven but by a heat which makes the bottom of the vessel containing it red, and which, being infusible in warm water, remains on the leather through which the phosphorus is pressed: the black powder which some chemists have separated from phosphorus, probably contains a much greater proportion of charcoal: I

\* Ann. de Chim. Tom. XXXV.

have found, by distilling phosphorus, which was transparent, twice successively, that it left some of this powder in the retort, but in a greater quantity by the first operation than by the second.

Mussin Puschkin observed\*, that on boiling the best purified phosphorus with acidulous carbonate of pot-ash, or even with the earthy and metallic muriates, and the nitro-muriates of metals, that a carbonaceous substance was always separated from it.

293. We have seen that phosphorus formed a combination with hidrogen gas, which is inflammable at a low temperature, when its proportion is sufficiently great: it also combines with azote; but although the phosphorus appears to enter into phosphurated azote only in a small proportion, it is inflammable at a low temperature; at least we do not know of any at which it ceases to be so†. This property depends on the weakness of the action of the azote, which is sufficient to dissolve the phosphorus, and give it the gazeous state, but which cannot retain it against the action of oxygen. In day-light phosphurated azote yields white vapours, which are owing to the combustion, and are luminous in the dark, as soon as it comes into contact with the smallest particle of oxygen, either free, or even in a state of solution; thus it is equally luminous when it is agitated with boiling

\* Ann. de Chim. Tom. XXIII.

† Journ. de l'Ecole Polytech. 3e cahier.

or distilled water. Phosphorus increases the dimensions of the azote in which it is dissolved: I have estimated this dilatation at nearly  $\frac{1}{40}$  of the volume of the azote gas (251).

Phosphorus acts otherwise with oxygen gas; because having a stronger affinity for it, it does not dissolve in it, at a low temperature, but it absorbs it exactly in the same manner as sulphuric acid, instead of dissolving in humid air, notwithstanding its tension, attracts the humidity of the air (245). This oxidation is not only made at the expense of the oxygen with which it is in contact, or which is in solution in the water, but also by the decomposition of the water, as has been observed before, if oxygen, less strongly combined, does not satisfy the action of the phosphorus. This oxide of phosphorus is also formed when its combustion cannot be completed, and then it is red: there generally remains some of this red oxide after the combustion of phosphorus. It is not known what proportion of oxygen the phosphorus can take in this state, or what is the difference in this respect between that which is most oxidized and phosphoreous acid: it is probable that the interval between their compositions is, but small.

When the temperature approaches the twentieth degree of Reaumer's thermometer, the oxygen gas becomes luminous, the phosphorus burns, and phosphoreous acid is formed; finally, when the temperature is raised nearly to  $30^{\circ}$  the deflagration becomes much more vivid, the combustion is  
more

more complete, and the acid approaches much nearer to the state of saturation, in respect of the oxygen.

The combination begins at a lower temperature in atmospheric air than in oxygen gas, because the azote dissolves a part of the phosphorus which then burns immediately; the heat which results gradually raises the temperature, and by that means the immediate combustion succeeds to the first: it is to avoid this second combustion, and to convert the phosphorus tranquilly into phosphoreous acid, that Sage, and particularly Pelletier, contrived their apparatuses, in which the access of air being rendered difficult, its action on the divided phosphorus cannot be sufficiently brisk to raise the temperature to the degree necessary for the direct inflammation; so that it is effected by the intermedium of azote: on this depends the peculiar property of phosphorus of being capable of combustion with more facility in atmospheric air than in oxygen gas: it is from this indirect combustion that the white vapours arise which precede the deflagration of phosphorus placed in atmospheric air.

294. When phosphorated hidrogen gas inflames, it is with the phosphorus, which opposes little resistance by its elasticity, that the combustion commences, when it is in a sufficient proportion, although the hidrogen shows a superior affinity, not only by the state of saturation which it produces, but also by the accidents of the combustion;

bustion; for if there is not a sufficiency of oxygen to produce both combinations, the water is formed in preference, and a portion of phosphorus is precipitated; nevertheless it is probably then in the state of oxide: the phosphorus is also precipitated when a solution of phosphurated hydrogen is decomposed by an insufficient quantity of oxygenated muriatic acid.

The properties of sulphurated hydrogen and phosphurated hydrogen prove that sulphur and phosphorus have great analogy with carbon; nevertheless they appear to have a much weaker affinity for hydrogen, for they can be easily separated from it, while insulated charcoal always retains it in combination, and the hydrogen readily permits a part to precipitate during combustion, while this effect is not observed with carburated hydrogen, unless there is a great proportion of carbon, and even in this case it retains a portion in precipitating (281).

It is probable that charcoal is indebted to this more powerful affinity, for the property of forming a gas composed of three elements, and of entering into vegetable and animal substances, which are for the most part compounds of different proportions of the same three substances; nevertheless it must not be considered as proved that oxi-sulphurated and oxi-phosphurated hydrogens are not formed in some circumstances: Gengembre even reports that when successive portions of phosphurated hydrogen gas are burnt, the last yield a green flame,



flame, which seems to announce a different composition.

295. The stronger affinity of phosphorus for oxygen, which will be more particularly established in the following chapter, explains the differences which distinguish the properties of the phosphurated and sulphurated hydrogen gases, as combustibles, but they have another distinctive character; sulphurated hydrogen combines with the alkalis like the acids themselves, and by that gives rise to the hidro-sulphurets; when it is formed by the action of water on the sulphurets, it remains in combination, and produces hidrogenated sulphurets.

Phosphorated hidrogen, on the contrary, has so little action on the alkalis, that its own elasticity is sufficient to prevent it from forming a combination with them: hence there are no hidro-phosphurets or hidrogenated phosphurets, analogous to the hidro-sulphurets and hidrogenated sulphurets, but the gas is disengaged as the phosphurated hydrogen is produced.

The rationale of this difference is to be found in the properties of the sulphur and phosphorus themselves: sulphur has a strong affinity for the alkalis, and, agreeably to the remark of Kirwan, might be assimilated with the acids, if it was not naturally in the concrete state: phosphorus, on the contrary, has but little action on the alkalis, and hitherto only the combination it forms with lime, which is very weak, and that, still doubtful, with ammo-

nia, have been recognized; it is therefore natural that the properties found in sulphurated hydrogen and phosphurated hydrogen, which are produced by an affinity without much energy, should be derived from an element which gives them its dispositions. The base which has the most inflammability gives the most of it to the gas which it composes, and that which has a greater disposition to acidity communicates the most of it to the gas derived from it: both may produce compounds much more variable in their proportions than those which they form with oxygen, because their affinity for hydrogen being much weaker, their combination with the latter does not produce a condensation which can occasion an interval between the proportions which may unite: these combinations retain their predominant affinity for oxygen, which decomposes them either directly, or by quitting another substance: then the elementary affinities replace the resulting affinity of the compounds; the base is acidified, and the hydrogen produces water.

## SECTION II.

*Of Binary Acids considered with Respect to their Composition.*

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## CHAP. I.

*Of the Sulphureous, and Sulphuric; Phosphoreous, and Phosphoric Acids.*

296. ALL the acids follow the same laws of combination while they experience no change in their composition, or in the constitution which is peculiar to them: we have, principally, employed the series of phenomena which they offer in this respect, to determine the laws of combination (*Sect. II. Part I.*), whose effects we must afterwards discriminate in the more complicated phenomena: but such of the acids as are capable of varying in their elements, receive particular properties according to the number and to the proportion of these elements, and the proportion is dependent on the forces which tend to form or to destroy the combination: we shall now compare the acids under these relations of composition.

The

The muriatic and fluoric acids are the only ones among those known which are immutable in their composition: the fluoric, which seems to be the most powerful of the acids, has hitherto been little examined by chemists; but every thing known of it obliges us to consider it as a simple substance: with respect to the muriatic acid, its natural production, which seems generally to accompany that of the nitric acid, and some other circumstances, show a state of composition in it; but it is not the less true that in all the known effects, except a very small number of instances, still doubtful, it does not experience decomposition, and consequently, in the explanation of nearly all the phenomena in which it participates, it is indifferent whether it is a simple or a compound substance.

The boracic acid has also been considered as a simple substance; but some chemists are of opinion that they have decomposed it, and it has been announced that Fabroni has determined its elements, and that he found that it owed its acidity to muriatic acid: till this philosopher has published his experiments we still consider the action of this acid in its known effects as that of a simple substance.

All the other acids owe their acidity to oxygen: no other exceptions can yet be shown but that of sulphurated hydrogen, which has the characteristic properties of the acids without containing oxygen, and that of the Prussic acid: but, 1st, sulphurated  
hydrogen

hydrogen seems to owe its acid properties to the sulphur in which the force of cohesion rendered them latent (295), and its predominant properties assign it a different class from that of the acids; 2d, Prussic acid has peculiar properties which do not permit its being blended with the acids.

The compound acids may be distinguished from each other, not only by the number of the elements, but also by the properties which some of them possess, of being capable of taking different proportions, and, by that means, acquiring different properties connected with these proportions; while there are some which can only form one acid combination, and whose elements pass into combinations of a different character when the resulting affinity is superseded by the elementary affinities.

In this section I purpose to examine such of the acids as are composed of only two elements; to seek the origin of their properties in those of the substances which enter into their composition; to follow them into the combinations which they form; and to determine the differences which characterise them, when they experience changes in their proportions.

The binary acids, whose composition is well known, are the phosphoric, the phosphoreous, the sulphuric, the sulphureous, the nitric, the nitrous, the oxygenated muriatic, and the carbonic. There are also metallic acids whose composition is analogous to that of the preceding; but I have brought  
the



the properties of metals and their modifications into the same section: I have already described the principal properties of carbonic acid; I have also, in different parts of this work, examined the formation and the properties of the phosphoric, phosphoreous, sulphuric, and sulphureous acids; nevertheless I shall bring into one point of view the variations which they undergo in their composition; the changes of constitution which are the consequence of them; the relations which are found between their properties and those of their elements, and the combinations which they form with different bases.

297. Phosphorus and sulphur, which serve as the bases of the phosphoric and sulphuric acids, differ little in their natural dispositions; they have nearly the same specific gravity; phosphorus is volatilized in a small quantity, with water which is at the degree of ebullition; but, without the aid of the aqueous vapours, it requires, according to the observation of Pelletier,  $232^{\circ}$  of Reaumur's thermometer, which differs but little from the degree at which sulphur itself is reduced into vapours, so that in these respects sulphur and phosphorus do not offer any differences which can have a material influence on the properties of their compounds; the force of cohesion of sulphur also differs too little from that of phosphorus to be capable of explaining the difference of their inflammability; besides, when sulphur is brought into fusion, it also shows a great inferiority in the  
energy

energy with which it combines with oxygen. It is therefore in their comparative affinity for oxygen that the cause of their difference (182), as well as that of the combinations which they form with hydrogen, will be found: phosphorus exercises a much stronger action on oxygen than sulphur, as is proved by its greater combustibility, and by the proportion of oxygen which it can take; from this stronger action the oxygen is much more condensed in phosphoric acid than in sulphuric acid, and the base itself experiences a greater condensation: hence it arises that sulphuric acid retains a portion of volatility at a certain degree of heat, while phosphoric acid supports a strong fire, allows the exhalation of all the water with which it was united, and is reduced into a vitriform substance rather than volatilize; so that this compound of two substances, of which one is very volatile, and the other is so in a certain degree, in consequence of the condensation which results from their mutual action, is much more fixed than a similar combination in which the most volatile element is found in a smaller quantity. Hence also it arises that the phosphoric acid can maintain itself much better than the sulphuric acid, when it is supported by the resulting action of a base (184), and on this difference are founded the processes employed either to abstract the phosphorus from phosphates, or to decompose the sulphates.

298. Although the phosphoric acid retains oxygen much more powerfully than sulphuric acid, it  
is

is nevertheless decomposed when it is submitted to a great heat with charcoal, while the other escapes its action; so that only a very small part can be converted into sulphureous acid: this difference depends on the weaker condensation of the sulphuric acid, which is volatilized before the temperature is sufficiently raised; the phosphoric acid, on the contrary, will reach a temperature at which it yields its oxygen to the carbon, which forms a volatile acid with it; at the same time it retains a part of the charcoal in solution, and the hydrogen of the latter combines with a portion of the phosphorus, and forms phosphurated hydrogen gas: if the phosphoric acid is combined with a quantity of a fixed alkali sufficient to form a neutral salt, the resulting force of the combination, added to the affinity of the oxygen for the phosphorus, puts it in a state to resist the action of the charcoal, so that this is unable to decompose it. The phosphoric acid is therefore taken in its insulated state, or combined with ammonia, which can be separated from it by heat, or a portion of the base of phosphate of lime, is abstracted by means of sulphuric acid, so as to reduce it to the state of acidulous phosphate, and then all the portion of acid which exceeds the neutral state may be decomposed by charcoal, and gives phosphorus; the rest remains in the state of phosphate of lime: the phosphoric acid which is combined with a metallic oxide may also be decomposed, if the oxide, as that of lead, is not in the number of those which

retain

retain the oxygen strongly, because then the charcoal directs its action not only on the phosphoric acid, but also on the oxide, and besides the metal tends to combine with the phosphorus, and to remain in the state of phosphuret (*Note XIII*).

Although charcoal decomposes phosphoric acid, phosphorus has the property of decomposing carbonic acid in other circumstances, as is shown by the curious experiments of Tennant and Pearson\*; this is a striking example of the reciprocal decompositions, of which it is so difficult to deduce the exact consequences relative to the affinity of these substances, because different circumstances change the state of the forces which produce these effects.

If I compare the quantity of oxygen with which carbon combines in carbonic acid, with that of the phosphorus retained in phosphoric acid; if I observe that notwithstanding the greater proportion of oxygen, carbonic acid saturates a less quantity of an alkaline base, it seems to me indubitable that the first exercises a much more powerful affinity on the oxygen than phosphorus; but when this decomposes carbonic acid, the carbon retakes the hydrogen with which it has a powerful affinity; in this state it combines with the phosphorus, for which it has also an affinity; the action which the alkaline base exercises on the phosphoric acid concurs with the other affinities, so that the decomposition of the carbonic acid is the effect of several causes combined.

\* Philos. Trans. 1791. Ann. de Chim. Tom. XIII.

In the sulphates, the resulting force of the combination is not sufficient to maintain the sulphuric acid against the action of the charcoal; but according to the affinity of the base, the force of cohesion of the sulphate, and the degree of temperature required for its decomposition, carbonic acid gas and oxi-carburated hydrogen gas are produced, and the sulphur remains in combination with the alkali; so that the sulphuric acid which was preserved from decomposition by its volatility, shows, in this case, the inferiority of its affinity for oxygen.

299. The phosphoreous and sulphureous acids have been compared; but I think this comparison inaccurate to a certain extent; the sulphureous acid has fixed proportions, and consequently a determinate constitution, at least the differences observed in it may be considered as doubtful, and of little consequence; but the phosphoreous acid has only one term of combination which can be considered as constant, that in which it is found when it is formed by the intervention of azote gas: since its constitution differs but little from that of phosphoric acid, and as there is no sensible interval to distinguish them, it appears to me probable that phosphoreous acid may, by a gradual oxygenation, acquire the state of phosphoric acid.

Phosphoreous acid retains a stronger action on oxygen than the sulphureous acid; it is even capable of decomposing water in the manner of a phosphuret (291); for by submitting it to ebullition



lition, phosphurated hidrogen is disengaged : the acid which results from the direct combustion approaches nearer to a state of saturation as the deflagration has been more brisk, and it may be completed in a sufficient space of time by the simple contact of the air ; nevertheless the acid is seldom obtained, at once, in this state of saturation, and when it is boiled, it continues to throw out luminous jets ; but when condensed oxigen is employed to combine with the phosphorus, as in Lavoisier's process, in which it is formed by means of nitric acid, or in that of Pelletier, in which a current of oxigenated muriatic gas is directed into phosphorus in fusion under water, or when, according to Fourcroy, phosphorus is burnt in oxigenated muriatic gas, phosphoric acid is formed immediately.

Although sulphuric acid is more easily decomposed, as well as all its states of combination, there is, nevertheless, an interruption to this effect, when the substances which act on it have taken that portion of oxigen which makes the difference between the sulphuric and sulphureous acids : the caloric disengaged during this new combination, or that employed in the operation, restores the oxigen to the state in which it is capable of constituting sulphureous acid ; this, which owes its volatility to this state of the oxigen, escapes from the chemical action which requires an interval of time for its operation, particularly when it is already weakened, so that the decomposition of the  
sulphureous

sulphureous acid is stopped, although the opposite force which remains may be sufficient to accomplish it (191).

On account of its stronger action on oxygen, phosphorus is capable of decomposing sulphuric acid, by depriving it of its oxygen, particularly when its force of cohesion is diminished by means of heat; but the sulphuric acid is reduced into sulphureous acid, and at this term the decomposition ceases, because the heat augments the elasticity of the sulphureous acid, which is an obstacle to this combination, and, in the cold, the force of cohesion of the phosphorus is equally an opposing force to it, so that phosphorus itself cannot decompose sulphureous acid, according to the observation of Fourcroy and Vauquelin\*; but this effect is not owing to a superior affinity in the oxygen for the sulphur, and it may be conjectured that phosphoreous acid, which would not experience an obstacle from the cohesion, may effect the decomposition of the sulphureous acid, whose elasticity would not be increased by the heat.

Sulphureous acid containing the oxygen in a state of moderate dilatation, preserves more of the acid properties in proportion to the quantity of oxygen; but it retains the oxygen much less than the sulphuric acid, although there is a greater proportion of sulphur in it, so that some sub-

\* Journ. de l'Ecole Polytech. No. 4. p. 449.

stances, such as sulphurated hydrogen, and some of the metals, can deprive it of it, by precipitating the sulphur, and the condensed oxygen easily converts it into sulphuric acid (181, 182).

300. This conversion of sulphureous acid into sulphuric acid by condensed oxygen is effected with much more facility than by the elevation of the temperature. I have found that by passing sulphureous gas mixed with oxygen gas, through a red-hot tube, it did not experience any change, because then the oxygen gas also acquires a dilatation which opposes the combination. Nevertheless if the heat was sufficiently raised, and equal to that necessary for the immediate production of sulphuric acid, it does not appear doubtful to me that the sulphureous acid would be then changed into sulphuric acid.

Hydrogen gas acts more efficaciously on sulphureous gas with which it is passed through a red-hot tube : it decomposes it on account of the stronger affinity of the hydrogen for the oxygen.

When the sulphites are exposed to the air, the action of the base, which tends to condense the elements of the acid, favours the formation of sulphuric acid, and by means of this circumstance, the proportions in which the oxygen and sulphur exercise the strongest reciprocal action, may be established ; the elastic effort of the sulphureous acid which is opposed to it being diminished, it is enabled to saturate itself with oxygen, and to absorb

absorb that of the atmosphere, until it has passed into the state of sulphuric acid: the sulphites change therefore into sulphates; the force, or the quantity of the acidity is not changed by this, but the effects of the condensation are become much greater; nevertheless the insoluble sulphites admit of this effect with difficulty, because of the force of cohesion which is opposed to it.

Although phosphorus exercises a stronger action on oxygen, the phosphites, exposed to the air, are changed with much difficulty into phosphates, according to the observation of Fourcroy and Vauquelin, which appears to me to depend on the phosphoreous acid experiencing but little condensation in passing to the state of phosphoric acid, so that the saturation produced in the phosphites by the base, instead of disposing them, by a weak combination, to combine with a greater quantity of oxygen, becomes a more powerful obstacle by the cohesion; for, without the action of the base, the phosphoreous acid would be converted into phosphoric acid.

301. Thus, the distinctive properties of phosphoric acid and sulphuric acid, as well as the greater part of those of phosphurated hydrogen and sulphurated hydrogen (295), depend on the stronger action exercised by the oxygen on the phosphorus; on the greater proportion of oxygen which the latter can fix; and, on the greater condensation which results from it. When  
the

the sulphur has been able to receive all the action of the oxygen, its combination experiences a condensation which also gives to it a certain fixity; but this effect is conformable to the energy of the forces which are less powerful than those which produce the phosphoric acid. When there is only a certain proportion of oxygen the reciprocal action of the two elements produces a weaker effect, and a less considerable condensation; the sulphureous acid retains an elastic disposition which constitutes its principal differences, either from the sulphuric acid, or from the phosphoreous and phosphoric acids. The affinity resulting from the alkaline bases supports the combinations (184), but likewise with more force in the phosphates and phosphites than in the sulphates and sulphites.

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## CHAP. II.

### *the Nitric Acid and its Modifications.*

302. THE combination of azote and oxygen, which forms the nitric acid, being produced from two substances which have nearly the same specific gravity, and the same disposition to elasticity, and which do not exercise a very energetic reciprocal action, is capable of receiving different pro-



portions, from whence several distinct combinations result, which, themselves, have the property of disuniting, or of forming other mixed combinations. From this arises a great variety of substances, and of changes of state, which render the history of nitric acid difficult to trace: the nomenclature by which its different states are indicated, necessarily participates in this obscurity of ideas, and the difficulty is increased because the combinations, the properties of nitric acid, and its numerous applications, have given rise to a multitude of experiments, some of which are contradictory. In tracing the modifications of this acid and their properties, I shall not, therefore, flatter myself with collecting all the results which are interesting, in the present state of our knowledge, by their importance in the production and explanation of chemical phenomena.

Priestley made a great number of experiments on nitrous gas, whose properties I shall first describe. It had been discovered that nitric acid contained a considerable proportion of oxygen; Lavoisier had established that by mixing oxygen gas and nitrous gas, the composition of which he had not determined, nitric acid was produced, which induced him to consider nitrous gas and oxygen gas as the two elements of this acid, and he had endeavoured to determine the proportions: but it was the celebrated Cavendish who made known the composition of nitric acid, and, consequently, that of nitrous gas, by forming this  
acid

acid by a continued action of the electric spark on a mixture of oxygen gas and azote gas\* ; since then, our ideas of the composition of this gas and the different combinations of its elements have been fixed, although the limits which separate them, and the properties which characterize each species of the compound, are not yet wholly free from obscurity.

According to Kirwan, the specific gravity of nitrous gas is 54, that of oxygen gas being 50 ; and, according to Davy, it is only 50, oxygen gas being 51. Although there is this small difference, it results from thence that oxygen gas and azote gas only experience a weak condensation by combining, whence it may be concluded that the decomposition of nitrous gas, and its transition to other states of combination, will not experience a great obstacle in the common circumstances.

Nitrous gas dissolves in water, as has been remarked by Priestley : Cavendish also noticed this absorption, and determined its influence in eudiometric experiments† ; he found that distilled water produced a greater diminution in nitrous gas, than that which had already been used to confine it ; that water which had been in contact with oxygen gas for a week, absorbed much more than that which had been kept during the same

\* Philos. Trans. 1785.

† *Ibid.* 1783.

space of time with azote gas : to this absorption he attributed the diminution observed on agitating nitrous gas with the purest azote gas.

From this it is manifest that it is only to the oxygen gas which is in solution in common water, and of which distilled water is not deprived, as is proved by its property of rendering phosphurated azote luminous (293), that the slight acidity it acquires by long agitation with a considerable quantity of nitrous gas is owing, and that the great difference observed by Cavendish between water which had been kept with oxygen gas, and that which had remained with azote gas, proceeds from this oxygen ; but water has not the property of decomposing nitrous gas, as was believed by myself and other chemists, and the great absorptions observed by Priestley should be attributed to the proportions of water and gas on which he experimented.

Davy, to whom we are indebted for some profound researches on the nitric acid and its modifications\*, says, that 100 measures of pure water, which has been boiled, can absorb 11.8 of nitrous gas ; that it does not then acquire any taste, and does not redden vegetable blues ; that if it contains salts with an earthy base, it absorbs less ; that it also takes a smaller quantity, if it holds carbonic acid, or any other gas in solution ; and that at the temperature of boiling water, nitrous

\* Researches, Chemical and Philosophical, &c. Bibl. Brit.

gas cannot remain united with water ; whence it may be concluded that the action of water can only slightly weaken the elasticity of this gas, and a small increase of it will be sufficient to produce their entire separation.

Nitrous gas dissolves easily and abundantly in nitric acid, which passes from blue to green, and to orange, according to the proportion of gas and that of water ; when it is concentrated it reaches as far as the rutilant state, so that the gas can combine in a quantity so much the greater, as that of the water united to the nitric acid is less, and, that water added to a rutilating nitrous acid drives off the nitrous gas in proportion to its quantity ; nevertheless it can only exclude it in part. According to Davy, 100 parts of yellow acid contain 2.75 of nitrous gas ; the specific gravity of the acid diminishes, and the caloric is disengaged during the combination : hence it results, 1st. that it is the nitric acid which tends to combine with the nitrous gas, and that the action of the water must be considered as opposed to this combination ; 2d. that the quantity of nitrous gas which can combine being limited by that of the water, the acid produced by the combination of nitrous gas and oxygen gas will retain a variable quantity of nitrous gas according to the quantity of water employed in the operation, and unquestionably according to the temperature.

When the acid holding the nitrous gas in solution is exposed to atmospheric air, it absorbs oxygen,

oxygen, according to the observation of the Dutch chemists\* ; after that the alkalis do not disengage nitrous gas, so that it is changed into nitric acid ; the nitrites seem also to have this property.

The alkalis, and also all the substances which exercise a brisk action on nitric acid, drive off the nitrous gas at first, because they have but little affinity with it, and the combination which they form has still less : heat acts in the same manner, because nitrous gas is much more expansible than nitric acid, whose solvent power is no longer sufficient to retain it.

303. Nitrous gas not only dissolves in nitric acid, but it is seen by some experiments of Priestley, that when its quantity is sufficient, its affinity gives such an increase to the force of the natural tension of the acid, that it can reduce it wholly into gas : this gaseous solution, which retains the rutilating colour must be distinguished from nitrous gas ; it forms what was called by Priestley nitrous vapour, and it may be immediately obtained from nitrous gas and oxygen gas ; but many variations are found in the composition of nitrous vapour.

When nitrous gas is mixed with oxygen gas over mercury, the mixture becomes rutilant, and its volume experiences only a slight diminution ; this is nitrous vapour ; but if the operation is per-

\* Recher. sur quelques prop. de l'acide nitreux. Journ. de Van Mons.



formed over water, suitable proportions of the two gases are quickly absorbed, and form nitric acid : hence it may be concluded, as was observed by Humboldt†, that the action of water is essential to the completion of the combination of the azote and oxygen which form the nitric acid : without it the nitrous vapour produces only a gaseous combination, which is not limited to fixed proportions, but will vary according to the proportions of oxygen gas.

When nitrate of pot-ash is decomposed by sulphuric acid, the vapour which is disengaged at first is rutilant, as was observed by Priestley, afterwards the colour disappears, and it is again produced towards the end of the operation ; because the action of the sulphuric acid on the base, and on the water, at first brings a portion of the nitric acid to a state similar to that of the preceding gas, which is formed by the mixture of nitrous gas and oxygen ; afterwards the heat volatilizes some water, which determines the composition of the nitric acid, which passes colourless in the distillation ; but towards the end, the water which could volatilize being exhausted, nitrous vapour is again formed, and the ruddy colour reappears

When the action of a metal disengages nitrous gas, especially when this action is brisk, the gas carries with it in solution a certain proportion of

† Ann. de Chim. Tom. XXVIII. p. 152.

nitric acid, and it also takes the ruddy colour: if it is passed through water it deposits this acid, which, in its turn, retains a portion of nitrous gas; but if it is received immediately over mercury, it retains the nitric acid, and forms also a nitrous vapour, so that it remains ruddy; if it has taken a little water with it, it loses its colour at a low temperature, and recovers it by means of heat: when the vapour of water is passed into this ruddy gas, as was done by Priestley, it becomes discoloured. It is evident therefore, 1st, that nitric acid, in taking the gaseous form by the action of nitrous gas, loses its characteristic properties by the combination which it forms with it, and that it is changed into nitrous vapour: 2d, that it is also changed into nitrous vapour when it is disengaged from nitrate of pot-ash by sulphuric acid: 3d, that the nitrous vapour can exist, either with an excess of oxygen, or with an excess of nitrous gas: if, in the first case, which is that of the distillation of nitric acid, it is passed through water, it is oxygen gas which is disengaged; in the second, it is nitrous gas; in both, it is the nitric acid which resumes the liquid state by means of the water, and which retains nitrous gas: by adding a small quantity of water, the nitrous vapour takes the constitution of nitric acid without, at first, losing the gaseous state; but it requires a greater proportion, according as the temperature is more raised, either to maintain the nitric acid in the state of gas, or to

to render it liquid. When nitric acid is in the state of uncoloured gas, it may be rendered rutilant by an excess of nitrous gas, as was done by the Dutch chemists.

These data seem to me to explain the numerous observations that Priestley made on nitrous vapour, which must not be confounded with the combinations whose proportions are constant ; but which varies, as well as the products arising from it, according to the circumstances in which it is found.

304. Nitrous gas dissolves easily, but in small quantity, in sulphuric acid ; it gives it a purple brown colour, and is retained by it pretty strongly ; nitrous vapour with excess of nitrous gas dissolves abundantly in this acid, and has the property, as was observed by Priestley, of forming crystals with it at a temperature above that of the congelation of water.

Nitrous gas dissolves in small quantity in muriatic acid ; but this acid absorbs much nitrous vapour, which, according to Priestley, gives it the properties of an excellent nitro-muriatic acid, and which will actually form nitro-muriatic acid.

Although the affinity which produces nitrous gas has little energy, as is shown by the weak condensation which its elements experience, it nevertheless resists its decomposition with considerable force, as well as the sulphureous acid (300), when the substance which exercises its action on it, is in the gaseous state, and the elastic disposition

tion of both is augmented by heat, or when it is a substance which opposes solidity to a new combination: thus nitrous gas is not decomposed when it is submitted to the action of the electric spark with hydrogen gas; but Davy effected its combustion by submitting a mixture of nitrous gas, gaseous oxide of azote, and hydrogen gas, to the action of electricity; then the combustion of the gaseous oxide of azote occasions that of the nitrous gas, as we have seen that by augmenting the proportion of oxygen, or of hydrogen, the combustion of that, which from being in too small a proportion would have resisted the effect of the elasticity, is determined (249).

When nitrous gas is passed through a red-hot tube, even with a super-abundance of hydrogen gas, it does not experience decomposition: I have made the experiment with care, raising the heat as high as a glass tube coated with clay could bear it; this corresponds with the inability of electricity.

In this case, therefore, the resulting affinity preserves its force, even when the dilatation has become much superior to the condensation which is produced by the combination; it is difficult to decompose the nitrous gas by hydrogen, and yet if there is a sufficient quantity of hydrogen with the oxygen and azote, neither nitrous gas, nor nitric acid are formed (266); but this maintenance of the resulting force is only found in substances whose elements have an equal dilatability, and the  
weakness

weakness of the contraction of the oxygen and azote contributes to preserve their combination during the dilatation by the heat, so that from this circumstance, a resulting affinity which, as the following facts will prove, is weak, resists the opposing action of heat much more than that which, being more energetic, would have produced a greater condensation; nevertheless there can be no doubt that the decomposition of nitrous gas can be produced at a more elevated temperature, since Davy effected this decomposition by submitting a mixture of hydrogen gas, nitrous gas, and gaseous oxide of azote to electricity, which produced a sufficient elevation of temperature by its own combustion.

Nitrous gas is also undecomposable by sulphur: I passed it through the vapours of sulphur in a heated tube, without success, and Davy observed that inflamed sulphur is extinguished in it; according to him, phosphorus cannot be inflamed in nitrous gas, but if it is introduced into it in a state of ignition it burns with nearly as much vivacity as in oxygen gas: this chemist has decomposed nitrous gas by means of charcoal by bringing the focus of a burning glass upon it; by this means phosphorus inflames in it alone.

Having passed nitrous gas through fragments of ignited charcoal placed in a tube, it gave rise to an inflammable gas of a particular species: 100 measures of this gas required for their combustion, 50 parts of oxygen gas; they  
produced



produced 65 of carbonic acid, and the residue was 0.45.

This gas is analogous to the oxi-carburated hydrogen gas, and takes its rise in similar circumstances; nevertheless it differs from it by retaining a considerable proportion of the azote in combination; if this azote is abstracted, it requires a greater quantity of oxygen for its combustion; it burns with a white flame, while the oxi-carburated gas gives a blue flame, even when it is mixed with azote gas. Perhaps greater differences may be found between their properties. Was it not this gas which Chaussier obtained by detonating three parts of nitre, or of oxygenated muriate of pot-ash, with one of charcoal\*, and which Cruikshank obtained from the detonation of common gunpowder?

Iron decomposes nitrous gas, even without the assistance of heat: the Dutch chemists found that after a certain space of time it was changed into gaseous oxide of azote, and that at the end of some days only azote gas remained; it is probable that the oxide of azote was absorbed by the water, as they have shown that this takes place on other occasions, but the azote announces a complete decomposition of a part of the gas: Milner observed that by passing nitrous gas through a gun-barrel containing iron-filings, and which he had made red-hot, that a part of the gas experienced an entire decomposition, and that a part of it was

\* Journ. de l'Ecole. Polytech 11<sup>e</sup> cahier, p. 323,

converted into gaseous oxide of azote ; but that the latter, by again passing through the filings, was also decomposed ; so that, in this way, the nitrous gas might be entirely reduced into azote gas\*.

From the preceding observations it may be concluded that nitrous gas is entirely decomposed by some substances, or by the aid of some circumstances. There has been great variations on the products of this decomposition. Lavoisier, who first attempted to elucidate this subject, concluded from his experiments, that nitrous gas was formed of a little more than two parts, by weight, of oxygen, and one of azote, or nearly of two parts, in volume, of the first, and one of the second ; subsequent observations have proved that the proportion of oxygen in this valuation is too great.

Van Marum, by decomposing nitrous gas, which yields its oxygen to a metal, by the electric spark, reduced its volume to 0.46, and the residue was azote gas ; but he observes that a powder of a whitish yellow was formed, which must have contained a little acid, so that the proportion of oxygen is a little greater.

On decomposing nitrous gas by a mixture of iron-filings and sulphur, with a small quantity of water, I had 0.44 for the residue, but a little ammonia must have been formed which diminished the residue.

\* Philos. Trans. 1789.

Davy concluded from the results which he obtained from the combustion of charcoal, from that of phosphorus, and from the combustion of the mixture of gaseous oxide of azote and hydrogen gas, by electricity, that nitrous gas is composed of 44 ponderable parts of azote, and 56 of oxygen : this valuation appears to me to be the most accurate approximation which has been obtained.

305. Nitrous gas is absorbed by a solution of sulphate of iron which loses its transparency by it, and takes a blackish colour, as was first observed by Priestley.

This property has become very useful for separating nitrous gas from the other gaseous substances with which it may be blended : Humboldt was the first who employed it for this purpose ; but he concluded from his experiments that nitrous gas obtained by the usual methods, always contains a considerable proportion of azote gas, which he separated by this means : this quantity of azote gas is only to be attributed to the imperfection of the experiment, for having used suitable precaution, I had only a residue of a 37th, on submitting the nitrous gas obtained by the solution of copper, and which consequently was similar to that of Humboldt, to this test.

Davy is of opinion that the red sulphate does not absorb the nitrous gas, and that in the common sulphate, it is only that which is in the state of green sulphate which effects the absorption, in conformity with the opinion of Proust ; but I have  
passed

passed nitrous gas into a very oxidized sulphate, and it became black, nevertheless the first portions of the nitrous gas do not produce a perceptible effect. The rutilant acid, poured in very small quantity into a solution of iron, gives it the same colour as nitrous gas: nitric acid does the same, but a much larger quantity of it is required, and when the effect is produced, lime disengages nitrous gas, so that it is the nitrous gas which produces the phenomenon, though the immediate cause to which it is owing is not clearly perceived.

According to Davy, the absorbed gas does not experience any alteration at a low temperature; but notwithstanding the observations which he has made on this subject, Vauquelin and Humboldt seem to me to have proved\* that ammonia is immediately formed; that consequently there is a decomposition of the water; and that, at the same time, a part of the nitrous gas is converted into nitric acid: as soon as the solution is impregnated with nitrous gas, ammonia may be disengaged by lime, and, on precipitating the iron by an alkali, a nitrate is obtained: the decomposition therefore is commenced, but heat will further its progress. In fact, the nitrous gas is driven off by the heat, when the solution of iron has not been decomposed by an alkali, but all the quantity which was absorbed is not recovered, and what is obtained is mixed with azote gas. Vauquelin and Humboldt believed

\* Ann. de Chim. Tom. XXVIII.

that the azote had been absorbed, in that state, by the solution of iron, but it does not absorb azote; this manifestly arises from the decomposition which the nitrous gas has experienced.

The green, or little oxidized muriate of iron has also, according to the observation of Davy, the property of absorbing nitrous gas, and even more rapidly and more abundantly than the green sulphate.

306. When the nitrous gas does not experience a complete decomposition by the action of an oxygenable substance, it passes into another state of combination, and acquires a peculiar character; it forms that gas which is one of Priestley's numerous discoveries, and which, with the Dutch chemists, who first analyzed it, I call gaseous oxide of azote, or oxide of azote gas\*.

The vivacity with which this gas supports combustion made it believed, for a long time, that it contained more oxygen than nitrous gas, and seemed to justify the denomination of dephlogisticated nitrous gas, under which Priestley made it known, and which was changed into oxygenated nitrous gas: but the supposition on which this denomination was established, is not reconcileable with the action of the sulphurets and other oxygenable substances, which convert the nitrous gas into this species.

Davy, to whom we are indebted for an important work on this gas, has called it nitrous oxide;

\* Journ. de Phys. Tom. XLIII.



but this denomination only distinguishes it obscurely from nitrous gas, to which it has, besides, been given by Fourcroy, whose scientific productions are so widely dispersed, and have so great an authority in instruction : I see no reason for rejecting the name chosen by the chemists who first made known the characteristic differences in the composition of this gas, and which is sufficiently calculated to designate them.

Nitrous gas exposed to the action of iron and water, of alkaline sulphurets, of non-oxidized muriate of tin, of the sulphites of pot-ash, of sulphurated and phosphurated hydrogen gases, of ammonia and of copper, at first, experiences a diminution of its volume, and when the diminution ceases, it is found to be converted into gaseous oxide of azote ; at the same time the substance which produces this change has received the oxygen, thus the sulphite of pot-ash is converted into a sulphate.

The Dutch chemists say that by passing nitrous gas through the vapour of sulphur in a tube, it is converted into gaseous oxide of azote ; but, as I have already observed, I repeated this experiment without success : according to Davy, liquid sulphureous acid does not produce any change in nitrous gas ; I have had a contrary result : a slight circumstance is sometimes sufficient to decide or to prevent its formation ; besides, it requires a greater or less length of time, so that it is easy to discover differences according to the nature of the observations.

The Dutch chemists maintain that this gas is the sole result of the decomposition of nitrous gas by substances which can carry off its oxygen, and they are of opinion that when there is a residue of azote it arises from a mixture of it in the gas submitted to experiment, and that the gaseous oxide of azote which was formed has been entirely absorbed by the water with which it was in contact: in this I differ from their opinion.

In the experiment of which I have spoken (304), nitrous gas placed in contact with iron filings and sulphur was reduced to 0.44 of its volume; the residue offered only the properties of azote gas: only the difference of the specific gravities is wanting to give the proportions of the elements of nitrous gas which have been determined by Davy: in this experiment therefore the nitrous gas was entirely decomposed, and the only remaining doubt is on the very small portion which makes the difference I have noticed; and this is probably owing to a little ammonia which might have been formed.

The gaseous oxide of azote not only supports the light of a taper, but it also gives it a greater brilliancy, nearly similar to what is produced by oxygen gas, and, in like manner, a match recently extinguished rekindles in it with vivacity: charcoal, phosphorus, and sulphur do not burn in this gas, according to the Dutch chemists, and ignited charcoal is extinguished in it; whence they concluded that this gas only burnt by the assistance

ance of the hydrogen contained in the combustible substances, and by this they explained why it could not serve for respiration, into which carbon must enter in combination with oxygen; but Davy has proved that the combustion of inflamed charcoal continued in this gas with more vivacity than in atmospheric air; that sulphur, which yielded only a blue flame was extinguished in it, but when it was in a state of brisk combustion it continued to burn and took a vivid rose-coloured flame; that lighted phosphorus burnt in it with activity, as well as a fine wire terminated by a piece of ignited wood; that although it did not serve for the respiration of animals in which this vital function cannot admit of a change, such as birds, it nevertheless supported the respiration of man, to a certain point, sometimes offering remarkable phenomena of excitation, and producing carbonic acid; so that the opinion of the Dutch chemists in this respect cannot be maintained.

The gaseous oxide of azote dissolves easily in water, as was observed by Priestley, and it is disengaged from it by ebullition without having experienced any change; nevertheless its taste is slightly sweetened; it does not change blue vegetable colours; it does not experience any change by being mixed with oxygen gas or with nitrous gas; the alkalis dissolved in water do not absorb a greater quantity of it than water, but Davy observed that they combined with it when they were kept in contact at the instant of its formation:

the method which he employed consisted in mixing dried pot-ash or soda with the sulphite, while it decomposed the nitrous gas. This combination dissolves in water; it does not appear to dissolve in alcohol; it does not change the taste of alkalis; the gaseous oxide is driven from it by the acids, and by a heat equal to  $400^{\circ}$ . Fahr.; so that its properties show that it is very weak.

When this gas is passed through an ignited tube it is decomposed, and the tube takes the colour of the nitrous vapour, which is, in fact, formed: when this vapour is absorbed, the residue has, very nearly, the properties of atmospheric air, so that it may be supposed, without any sensible error, that it has the same proportions, and the dimensions of the gas are but little diminished; nevertheless the nitric acid which is formed only amounts, according to Davy, to two-tenths of its weight.

Electric shocks also change the nature of this gas: according to the Dutch chemists, it loses a sixth of its volume, and the residue is also similar to atmospheric air.

They observed that if a mixture of hydrogen gas and gaseous oxide of azote is submitted to the action of electricity, a detonation takes place: if the operation is made with one part of hydrogen gas and three parts of the other gas, all the hydrogen disappears, and the residue has the properties of atmospheric air; whence they conclude that 300 parts of this gas contain 50 of oxygen more than

than an equal quantity of atmospheric air ; but they were unable to carry their consequences further, because they were unacquainted with the specific gravity of the gaseous oxide of azote : they therefore consider the gaseous oxide of azote as occupying the last place in the series of substances which arise from the decomposition of nitrous gas ; they depend on the stronger affinity which the hidrogen gas shows for the oxigen, compared with that of carbon, to explain the difference of its properties from those of nitrous gas. Davy has shown that this difference disappeared at a high temperature, and he has explained the different phenomena offered by this gas, particularly in its formation and its decomposition, by the variations which he supposes in the mutual affinity of its elements, at different temperatures : but these alternate differences, which are supposed in the affinity of two elements having nearly the same dispositions, and which are not derived from the general properties of similar substances, appear to me to be only a vague manner of representing the results of observation.

According to the experiments of this able chemist the specific gravity of gaseous oxide of azote is to that of oxigen gas as 147 to 100, and on this datum and the results which he obtained from its decomposition by different means, but particularly by the decomposition by charcoal, he has determined that it is composed of 63 ponderable parts of azote and 37 of oxigen.

I have



I have also endeavoured to ascertain the specific gravity of this gas; I employed excellent instruments, but my result is remote from that of Davy. I found the proportion with oxygen to be only as 123.5 to 100. Nevertheless a part of the gas was absorbed by boiled water, nearly to a twentieth, and I took into the estimate the correction which this quantity requires: perhaps the gas is not constant in its composition. This difference prevents me, at present, from adopting Davy's results without reserve.

The method employed by the Dutch chemists to analyse this gas, by detonating three parts of it with one of hydrogen gas, seems to me the easiest and best calculated to make known its elements, when its specific gravity is determined; for the residue may be analysed with accuracy, and I think I have ascertained that there is not any acid formed in this operation, as stated by Davy: by making it over tincture of turnsole, its colour was not changed, even at the surface.

This gas may be destroyed by a great proportion of oxygen, but it appeared to me, by one experiment, that the quantity of azote then prevented the entire combustion of the oxygen; so that there remains a greater uncertainty than when the proportions indicated by the Dutch chemists are employed.

307. According to these observations, gaseous oxide of azote is a combination in which the oxygen is in a smaller proportion than in nitrous gas,

gas, but it is more condensed, because it experiences a stronger action from the azote.

It seems to me that these circumstances account for the characteristic properties of this gas, which may be reduced to the two following heads.

1st. The oxygen being subjected to a more powerful affinity than in the nitrous gas, it must offer more resistance to the action of the substances which tend to combine with it, while the constitution of the gaseous oxide of azote is not excited to change ; in fact, the gaseous oxide of azote neither burns charcoal, nor sulphur, nor even phosphorus which have not been raised to a high temperature: it cannot support respiration without difficulty, although the oxygen is in greater proportion in it than in atmospheric air : I have found that it was not changed by the action of a moistened mixture of sulphur and iron-filings, to which I left it exposed for a long time, and which entirely decomposes nitrous gas: it is therefore certain that it resists decomposition at a low temperature much more than nitrous gas (304).

2d. When it experiences the action of heat, on the contrary, it is decomposed more easily than nitrous gas, because the expansion which is the effect of it tends to restore the two gases which compose it, and which are condensed in it, to their natural state, while this expansion has little effect on nitrous gas whose two elements are not much condensed: by it the elements of the  
gaseous

gazeous oxide of azote are divided ; one part resumes the state of nitrous gas ; the other part is reduced into oxygen gas and azote gas, nearly in the proportions of atmospheric air : the continued action of electricity produces the same change, as well as in several other circumstances.

If, consequently, heat or electricity join their action to that of an oxygenable substance, it will yield its oxygen more easily than nitrous gas, and, considering the quantity found in a similar volume, and the rapidity of its decomposition, it produces appearances which approach those of oxygen gas.

308. Azote therefore offers two terms of saturation with oxygen, in which the condensation is more considerable than in the other degrees of saturation, as is remarked in several combinations (195). In one, the reciprocal saturation appears to produce a neutral state, this is the gazeous oxide of azote: in the other the oxygen predominates, and gives its characteristic properties to nitric acid, but this requires the concurrence of the action of water to be insulated.

Between these two combinations are nitrous vapour and nitrous gas: the first may receive very variable proportions ; but has the nitrous gas constant proportions, or are there intermediate states between the gazeous oxide of azote and it? I incline to the latter alternative, although the nitrous gas formed in different circumstances, has appeared to me to have a sufficiently

ciently uniform composition, but it is more especially by means of decomposition that it has seemed to experience variations in its elements.

When the purest nitrous gas has been submitted to the action of alkaline sulphurets, and after having made an essay of it with sulphate of iron, there is always a residue which is not soluble in water, and which consequently is not gaseous oxide of azote. The same nitrous gas which had yielded me a residue of only  $\frac{1}{37}$  with sulphate of iron, gave one of  $\frac{1}{20}$  with sulphuret of pot-ash : one part of the gas must therefore experience a total decomposition, while another changes into gaseous oxide of azote.

The total decomposition takes place when the moistened mixture of sulphur and iron-filings is employed, and when the nitrous gas is submitted to the action of electricity sufficiently prolonged, with the contact of a metal ; but can it be supposed that in these circumstances each molecule of the nitrous gas yields successively all its oxygen and experiences at once a complete separation ? It would be the same as to say that in a hygrometric substance, in a humid state, each hygrometric molecule yields successively all the water it held in solution, and passes from extreme humidity to the greatest drought ; or that in a heated body, the caloric raises each molecule at once to the highest temperature.

The observation of all chemical phenomena shows that chemical action is progressive, until  
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it meets with obstacles which require its accumulation that it may be able to overcome them.

It appears to me therefore probable that the decomposition of nitrous gas is successive, as far as the period of the production of gaseous oxide of azote, when the circumstances permit its formation: there it finds an interval which separates the nitrous gas from the gaseous oxide of azote, which takes a peculiar constitution: if the force which decomposes the nitrous gas has sufficient energy, the gaseous oxide of azote cannot be formed; but when it can receive its constitution, it maintains it against the causes which might have continued the decomposition of the nitrous gas, until this loses its advantages by an elevation of temperature.

Priestley, and the Dutch chemists, who have noticed the effect of iron-filings and sulphur on nitrous gas, think that the residue of azote which they obtained was already in the nitrous gas they made use of, so that the gaseous oxide of azote which is formed must have been entirely absorbed by the water with which it was in contact; consequently they do not distinguish the manner in which the sulphur and iron act, from that of the alkaline sulphurets: but, in the experiment which I have already mentioned, I used a nitrous gas which did not leave me any appreciable residue with a solution of sulphate of iron, so that the residue of 0.44 of azote which I had obtained must be attributed to its decomposition alone: with respect



spect to the formation of gaseous oxide of azote, which did not take place in my experiment, I attribute the difference of our results to my having employed but a very little water in it; when the mixture of sulphur and of iron is diluted with a certain quantity of water, the intervention of the water will render its action on the gas weaker, and then this mixture can produce effects analogous to those of the alkaline sulphurets; there is, however, always a difference in the quantity of the residue, which is much more considerable with the iron and sulphur, as may be ascertained by a comparison of the results of all the experiments that are described. The Dutch chemists estimate the residue at a fourth of the primitive volume of nitrous gas.

The substances which produce gaseous oxide of azote also decompose the nitrous gas in part; hence it arises that a residue is found which exceeds that obtained by dissolving nitrous gas with sulphate of iron.

I also employed sulphate of iron to examine what passed at the commencement of the action of a sulphuret on nitrous gas; I took the period at which it had experienced a diminution of nearly a sixth of its volume: agitated with water, it experienced a slight diminution, so that gaseous oxide of azote was already formed; after that it left a residue at least double that which the same gas would have given before the action of the sulphuret.

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This immediate decomposition of nitrous gas will vary according to the energy of all the means employed, and according to the circumstances which favour it.

309. When the metals decompose nitrous acid they produce nitrous gas, gaseous oxide of azote, or a mixture of the two, according to the energy which is peculiar to them, and also according to the circumstances which accompany their action: zinc and tin, which have the property of decomposing water by the great action they exercise on the oxygen, produce only gaseous oxide, especially when their action is not very brisk, and the acid is diluted with a certain quantity of water; but when the acid is concentrated, the disengaged gas contains a small proportion of nitrous gas, particularly with zinc: the Dutch chemists establish it as a general fact, that the metals which decompose water, form nitrous gas when the acid is very concentrated, and, on the contrary, give rise to gaseous oxide of azote when the acid is mixed with a certain quantity of water: they are of opinion that the water is then decomposed by the metal, and that its hydrogen decomposes the nitrous gas to form water with a portion of its oxygen: this is to attribute two opposite effects, the composition and decomposition of water, to the same cause, and in the same circumstances: besides I am convinced that, in the greatest state of concentration of the acid, it is still gaseous oxide of azote which is formed, and if a small portion of nitrous gas is disengaged

gaged at the same time, it seems to me to arise from this, that in the very brisk, and necessarily unequal action, a little nitrous gas is formed, which escapes: this vivacity of action produces also another effect, the gaseous oxide of azote which is obtained is mixed with a greater or less proportion of azote gas, which, on the contrary, proceeds from a portion of the nitric acid having been entirely decomposed. When therefore it is wished to obtain gaseous oxide of azote, in a state of purity, by means of zinc and tin, it is requisite to employ a weakened acid, that the action may be restricted to the regular production of this gas, and not furnish the water necessary to its composition: a part of the water is nevertheless decomposed by the same energetic action as produces the gaseous oxide of azote, as is shown by the ammonia which always accompanies its formation: but these two productions are simultaneous.

Iron produces nitrous gas and gaseous oxide of azote, or rather a variable mixture of these two gases, and it appears that it is its proportion and its state of division which more immediately determine the nature of the product; the concentration of the acid seems to me to have much less influence, and I have not found, as is asserted by the Dutch chemists, that nitrous gas is obtained when the acid is very concentrated. One method of obtaining a great quantity of gaseous oxide of azote, by the intermedium of iron, is to throw filings of the metal into a nitric solution of  
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it ; a brisk effervescence is quickly established ; a great quantity of gaseous oxide of azote is disengaged, and the iron passes to the state of black oxide.

I do not know what is the cause of the energy with which the iron acts in this case, but a proof of it is, that there is at the same time a considerable production of ammonia.

The other metals, such as bismuth, copper, lead, mercury, silver, yield, in every case, only nitrous gas, and at the same time no production of ammonia is observed, even with bismuth, although it produces a brisk effervescence, whereas the first form a quantity which is sometimes considerable.

310. It is evident that the gaseous oxide of azote may owe its origin ; 1st, to nitrous gas, when a substance is capable of carrying off part of its oxygen, without, however, exercising an action so brisk as to produce its total decomposition ; 2d, to the immediate action of a metal on nitric acid, when the metal has sufficient power in itself to push the decomposition of the acid to the necessary term : then ammonia is always formed, which is also a product of the necessary degree of action.

There is also another circumstance in which the gaseous oxide of azote is produced ; it is from the decomposition of nitrate of ammonia by heat, as I have shown long ago\* ; and it is in this manner that it is obtained for the experiments,

\* Mém. de l'Acad. des Sciences, 1785.

which

which are at present so much multiplied on the singular effects which are sometimes occasioned by respiring it: in this decomposition, the hydrogen of the ammonia combines with the excess of the oxygen of the nitric acid, and produces water: thus by an effect of different circumstances there is a decomposition of water when this gas is formed by the action of metals on nitric acid, and, in this case, it is a consequence of the formation of water: it is thus that ammonia sometimes gives birth to nitrous gas, and, on the contrary, in other circumstances arises from the decomposition of nitrous gas\*: a new example of the circumspection required in judging of the affinity of a substance by the products of an operation, in which the chemical action is complicated with conditions which may modify its effects.

Even the results of this operation, which have been analysed with much care by Davy, offer some variety according to the circumstances: if the decomposition is made too suddenly, the gas obtained is partly nitrous gas, as we have seen this effect take place when the metals decomposed nitric acid too rapidly; and the circumstance which must be most particularly attended to, when it is wanted in a state of purity, is the temperature, which must only be sufficient for the decomposition of nitrate of ammonia.

§11. Nitrous gas, in combining with oxygen to reproduce nitric acid, requires proportions of ox-

\* Séances des Ecoles Normales.



gen which vary greatly according to the circumstances in which this combination is formed, and occasion the reproduced acid to be more or less removed from the state of nitric acid, or to contain more or less nitrous gas.

Lavoisier, who had not paid attention to this difference, endeavoured to determine the proportions of oxygen and nitrous gas which combine to form nitric acid, and he concluded from his experiments, that the nitrous gas in it was to the oxygen as 69 to 40. From this has been deduced the proportion of oxygen which was absorbed by the nitrous gas, in the examination of the air with Fontana's eudiometer, and Humboldt has endeavoured to bring the results to this term by deducting from the volume of the residue a quantity of azote gas which he supposed to be always mixed with nitrous gas; but this supposition is unfounded, since nitrous gas, prepared with sufficient care, is absorbed nearly without residue, either by the sulphate or by the oxygenated muriatic gas.

Nevertheless Fontana and Ingenhouz have observed that a great number of circumstances might augment or diminish the effects of nitrous gas; and Cavendish has determined several of them with that precision which characterizes him (248); I shall add here the result of some experiments which I have made on this subject.

To make the combination of oxygen gas and nitrous gas, it is necessary to employ nitrous gas which has been so prepared that it could not mix  
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with atmospheric air, in order to guard against the effects which would result from this mixture; the copper, which is the substance usually employed, must therefore be put with the acid into a flask, which must be completely filled with the liquid.

When the nitrous gas is put first into the tube in which the mixture is made, there is a much more considerable absorption: 46 measures of nitrous gas mixed in this manner with 15 successive measures of oxygen gas left only two measures, and this residue being tried in Volta's eudiometer with hydrogen gas, detonated and left a residue which scarcely indicated one measure. This experiment also shows how unfounded is the supposition of a residue left by nitrous gas; in this instance only the sixtieth part of the volume of the two gases was obtained, a quantity so small as to be incapable of establishing any result: the oxygen gas must have contributed a small part of it, and the water in which the operation was performed might have furnished the remainder, or nearly so: nitrous gas must therefore be considered as combining entirely with oxygen gas, when both are very pure; but their proportions may be varied by different circumstances.

Twelve measures of oxygen gas, put first into the same vessel, absorbed only 24 of nitrous gas, so that in this instance, the acid which was formed contained less nitrous gas: these two experiments were made with a cylinder of considerable diameter: three measures of oxygen gas put into the narrow tube which forms Fontana's eudiometer,

ter, absorbed only about five measures of nitrous gas; consequently the same gases yield very different products according to the order in which they are introduced, and according to the capacity of the vessels in which the mixture is made; the agitation which is employed and the temperature have also an influence on the result; finally, the water made use of may occasion a variation, if it contains a carbonate, whose carbonic acid, as was noticed by Humboldt himself, by disengaging and combining with the gaseous part, will increase the residue.

If, instead of oxygen gas, a mixture of determinate proportions of azote gas and oxygen gas is made use of, it will be found that the quantities of nitrous gas will vary according to these proportions, so that it will require more of it when the azote gas is in a greater proportion, and nevertheless the diminution of the volume compared with the quantity of the oxygen is so much the less: this is because the azote retains a portion of the nitrous gas and even of the oxygen gas, in the gaseous state, a quantity which increases its own. It is evident, therefore, how deceitful the inductions are which are drawn from the action of nitrous gas on atmospheric air, to determine the proportions of oxygen gas found in it (248).

The irregularity in the effects of nitrous gas depend, 1st, on the acid which is formed retaining more or less nitrous gas in solution, according to the circumstances; 2d, on the gases which may be  
disengaged

disengaged from the water ; 3d, on the action by which the residue retains a portion of nitrous gas, and probably of oxygen gas.

Notwithstanding these numerous causes of uncertainty, Davy employed the absorption of oxygen gas by nitrous gas to determine the composition of nitric acid ; but he examined the liquid product, he valued the nitrous gas which it held in solution, and by a laborious process which required all his accuracy, and all his patience, he succeeded in ascertaining the proportions of these two substances in the different states of the acid.

The quantity of oxygen which causes the difference of nitrous gas and nitric acid may be easily determined, by attending to the known proportions of oxygen gas and azote gas, which compose nitrous gas (304), and to the formation of nitric acid by the action of electricity. Nitrous gas contains 44 ponderable parts of azote, and 56 of oxygen : in the second experiment by which Cavendish formed nitric acid, by the immediate combination of azote and oxygen, and which it is proper to select, because it is that which gives the greatest proportion of oxygen, and consequently the acid retained less nitrous gas foreign to its composition, the proportion of oxygen was to that of azote, as 253 to 100.

But if the weights of these two gases are taken instead of their volume, it will be found that 100 parts of nitric acid are formed of 25 of azote, and 75 of oxygen, nearly.

The acid which Cavendish formed could not have been entirely in the state of nitric acid, as he observed himself: it must have held a little nitrous gas in solution: but this can occasion but very little difference in the proportions, as is shown by Davy.

It seems to me therefore that, though this valuation cannot be considered as rigorously correct, it is an approximation sufficient for the explanation of most phenomena.

312. When the nitrates are exposed to a strong heat, the elements of the acid acquire a degree of tension which separates them from the alkaline base: at this high temperature they take all the caloric which is required for each of them; they therefore separate, or are only retained in that feeble state of combination which constitutes solution: but some nitrates at first permit the disengagement of a greater or less portion of nitric acid; this is probably on account of the water which they hold more strongly than the others, and whose action retains the acid with which it is volatilized (303).

When nitric acid is decomposed in this manner, oxygen gas is disengaged, almost alone, at the commencement, because it predominates in the combination, and its excess will yield more easily to the forces which tend to destroy it: the nitrates are thus changed into nitrites: some experiments of Priestley seem to prove that these have the faculty of attracting the oxygen of atmospheric air :  
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it may be conjectured that the nitrite of lime, changed in this manner into nitrate by the action of fire, owes the phosphorescent property which has caused it to receive the name of Baldwin's phosphorus, to this action on the oxygen of the atmosphere.

The nitrous acid which thus forms the nitrites, must not be confounded with that which arises from the saturation of nitric acid by nitrous gas: in the latter, the nitrous gas preserves a different state of condensation; it constitutes a peculiar substance, so that from its elasticity it is eliminated from the weak combination which it forms, by substances which enter into a more energetic combination with nitric acid: thus the alkalis drive it off, even water sets part of it free, so that only a certain proportion can remain, according to the quantity of the water, and according to the temperature (302): the difference of constitution which distinguishes these two acids depends, however, on so slight a circumstance, that if an acid is poured on a nitrite, nitrous gas is disengaged, or rather a nitrous vapour, similar to that which is formed by the union of nitric acid with nitrous gas.

The first of these acids cannot therefore produce nitrites, and its proportions experience great variations, according to the circumstances. It is only to the acid which forms nitrites that the denomination of nitrous acid belongs, as is very properly observed by Chenevix; and it would be expedient  
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to indicate the solution of nitrous gas in nitric acid only by some mark capable of distinguishing it, such as the colour: we should be contented to call it nitric acid, of a deeper or paler yellow, ruddy, &c.

§13. If the affinity of azote is compared to that of hydrogen for oxygen, an idea may be formed of the cause which produces the differences existing between their combinations: of all those of azote, the gaseous oxide is that in which the mutual properties are the most completely saturated; this gas dissolves in water, and scarcely communicates any sensible property to it; it is inodorous; it has only a slightly sweetish taste; it is not changed by nitrous gas or by oxygen gas, or by those substances which have the strongest tendency to oxygenation while the temperature is unchanged: in this respect it may be compared to water whose two elements are equally in a state of saturation: now it only requires 15 ponderable parts of hydrogen to produce 100 parts of water, while one part of oxygen requires nearly two of azote for saturation; whence it may be concluded that the affinity exercised by azote is much inferior to that of hydrogen.

Hence it follows that, by the same degree of saturation, azote will produce a much less condensation; in fact, gaseous oxide of azote remains a permanent gas: it also results from it that this combination is only separated by small intervals from other possible combinations of azote and oxygen,

oxygen, while the strong condensation experienced by that of the hydrogen can only admit of the formation of water (207).

With a greater proportion of oxygen, nitrous gas is obtained, in which the condensation is much less considerable, and which easily yields a part of its oxygen to pass to the state of gaseous oxide of azote, which is more constant: but we have seen that the difference of condensation is itself the cause which renders the gaseous oxide much more easy to decompose at an elevation of temperature which tends to restore the natural state to its elements, so that it then produces the phenomena of combustion with sulphur, phosphorus, and charcoal; while nitrous gas, in which the elements are but little condensed, preserves its constitution more easily in this circumstance (307).

On account of its having but a weak combination, nitrous gas can, with facility, enter into combination with oxygen, and in very variable proportions; but it retains the gaseous state in forming nitrous vapour; it is only by the action of water that the nitrous vapour, by separating from the superfluous part of the oxygen gas, or of the nitrous gas (303), is reduced to nitric acid: nevertheless, although the water exercises its action on the determinate proportions which form nitric acid, it can dissolve a variable proportion of nitrous gas, because the oxygen in it is far from being saturated with azote, and it then forms the yellow or the rutilant acid.

From

From what precedes. it results that it is that part of the oxygen, which makes the difference between the gaseous oxide and the nitric acid, which produces the effects of acidity; but as the oxygen is but weakly retained in it, it readily abandons a part to substances which have a tendency to oxygenation, to pass to the state of nitrous gas, when the action of the substance is weak, or to that of gaseous oxide of azote: this is not the case when the acid is combined with a base; it then resists its decomposition by the resulting force of the combination, until this force is destroyed, either by heat, or by a competition of affinities: in the action of nitric acid, there are only the affinity of the azote, and that of the water, which tend to maintain it; in a nitrate, the energy of the acidity, arising from the oxygen, becomes an additional force (184).

When the nitric acid is attached to a base, other substances produce different effects by their action, according to the character; if the acids exercise their action on the base, they act according to their respective quantity, their capacity for saturation, their fixity, or their volatility: the nitric acid separates, if the temperature requires it, and if it holds enough of water it retains that state, if not, the nitrous vapour, which can reproduce it, when water contributes to its condensation, is formed. But when it is an oxygenable substance which acts, it requires that the temperature should be so raised that the elements  
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of the nitric acid experience a dilatation, which weakens the resulting force of the alkaline base, and then the action being exercised on its elements, still greatly condensed, it produces a much more complete decomposition than in nitric acid simply combined with water : however, the effects vary according to the force which produces them. One part of sulphur, with four of nitrate of pot-ash, disengages much nitrous gas\*. Oxide of arsenic does the same, and it is probable that phosphorus, in a small quantity, would produce the same effect ; charcoal, in too great a proportion, produces a species of inflammable gas (304) : very variable results may be obtained, according to the difference of substances and of their proportions : sometimes the elevation of temperature disengages a portion of oxygen, even without its entering into combination, but it is reduced to the elastic state, so that a portion is often blended with the gas which is disengaged.

314. All the combinations of azote with oxygen retain the greatest part of the caloric which the oxygen gas possessed, so that when the acid is formed by the union of oxygen gas and nitrous gas, very little caloric is disengaged, as was ascertained by Laplace and Lavoisier, in the calorimeter ; and what proves that nitrous gas itself is possessed of much caloric, is that the effects produced by the nitrates show that all the oxygen

\* Mém. de l' Acad. 1781.

which



which enters into the composition of the acid is deprived of only a small portion of the caloric belonging to oxygen gas, and which it resumes when it is disengaged from the nitrates by the sole action of heat.

The effects of the detonation of nitrates are owing to the expansion produced by the caloric which makes the difference of the oxygen combined with the bases which produce it, from the same oxygen combined with azote: this explains the effects of gunpowder, and accounts for its composition: it must have a little sulphur, because this substance being more volatile, and more easily combustible than the charcoal, it will facilitate its inflammation; but although the heat disengaged from it be much more intense, the combustion of the sulphur would only have produced a sulphate, a substance fixed, or of much more difficult dilatability than carbonic acid. It requires therefore only a small proportion of sulphur which produces the first effect or augments the temperature: the violence of the expansion must arise principally from the production of carbonic acid and azote gas, in the ratio of their respective quantity.

Several philosophers have attributed all the effects of powder, which are owing to the expansion, to water reduced into vapours, and which, as Rumford has shown, are much more considerable than was believed by Robin; but an easy calculation, as has been observed by Laplace, will

will show that the heat produced by the detonation of nitre is very far from being sufficient to explain these effects by the expansion which it can produce in the vaporization of water, whatsoever maybe the quantity supposed to be in the powder. It is to the elastic tension of the carbonic acid which is set at liberty, or rather to that of the oxygen which enters into its composition, as well as to that of the azote gas, and to the augmentation of that tension by the heat which is disengaged, that they are principally owing: the quantity of water which might exist, or even that which is formed, can only contribute a very small part to it.

In this phenomenon, the carbonic acid which produces the detonation, is not in combination but in the gaseous state, because the temperature is too much raised for it to combine with the alkali: this explains an observation of Rumford; having detonated a small quantity of powder, in a close vessel, and, having opened it after cooling, there was only a little hissing, which announced but a small quantity of gas, which led him to explain the detonation by a different cause from the production of gas: during the cooling the carbonic acid had combined with the pot-ash. By this I explain another observation of Cruikshank\*. Having examined the matter which remains after the explosion of the powder, he found

\* Bibl. Brit. Tom. XVI. p. 72.

*that it was a compound of pot-ash, united to a small quantity of carbonic acid, of sulphate of pot-ash with a very small proportion of sulphuret of pot-ash, and of unconsumed charcoal: the carbonic acid which had been produced, was only fixed in a small quantity in this matter.*

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### CHAP. III.

#### *Of Oxigenated and Super-oxigenated Muriatic Acid.*

315. OXIGENATED muriatic acid, composed of two volatile elements, although with a different degree of elasticity, owes its existence only to the action of a weak affinity, and nevertheless both the elements of which it is composed have the property of forming energetic combinations with a great number of other substances.

The muriatic acid exercises too weak an action on the oxygen to counterbalance the force of the elasticity which it has in the state of gas, and it is only by the concurrence of the forces which tend to give the elastic state to the muriatic acid, and at the same time to the oxygen condensed in some substance, that it can be produced.

The

The state of dilatation in which the elements of this acid are found, and the weakness of their union, render them therefore but little calculated to form durable combinations, and the greater part of the substances which combine in preference, either with the muriatic acid, or with the oxygen, or even with both, decompose it, and unite either with one of its elements, or with the two, changing their state by the condensation: this is what happens with most of the oxigenable substances which rob it of the oxygen, sometimes without affecting the muriatic acid, at others, by combining, first with the oxygen, and afterwards with the muriatic acid\* ; but when a substance unites with the two elements without separating them, the oxigenated muriatic acid may pass suddenly into a different state, or this change may be gradual according to the force which produces it. Finally, in oxigenated muriatic acid, the oxygen preserves the caloric which belongs to the oxygen gas, at least as much as in nitric acid. These considerations will guide us in the explanation of all the phenomena which are owing to the action of oxigenated muriatic acid, and in which those arising from the combination of this acid with a base, must be distinguished from those produced by its decomposition, and by the combination of its elements.

\* Mém. de l' Acad. des Sciences, 1785.

In both the effects which it produces, the oxygenated muriatic acid shows much correspondence with the nitrous gas; but the cause of the differences which distinguish them may be found in their composition: nitrous gas, formed of two substances both of which have great elasticity, retains this property in a considerable degree; it only dissolves in water in a small proportion; and, in the proportions which form it, has not, sensibly, any acid quality: the oxygenated muriatic acid, one of whose elements has much less elastic disposition, dissolves with more ease in water; nevertheless it has only a weak affinity for this liquid, for a great part separates from it, by cold, and then takes the solid and crystalline state, so that it is rather the weakness of the elastic disposition than the force of the action of the water which produces this union, and as, of its two elements, one is naturally acid, and the other conveys acidity to the substances with which it combines, when it does not experience too great a saturation, it has a much brisker action on alkalis than on nitrous gas; but these condense it more or less, they change its chemical action, so that the effects vary according to the state of condensation to which it is reduced: these easy deviations in the power of the acidity render the effects much more unsettled, and more difficult to seize than those of the acids which are more uniform in their constitution.

The



The alkalis may therefore combine with oxygenated muriatic acid, whose powerful odour they cause to disappear, and whose colour they destroy; but it forms another species of combination with them, experiencing itself the change which constitutes it super-oxygenated.

The oxygenated muriates must therefore be distinguished from the super-oxygenated muriates. Chenevix, who has lately published some very interesting observations\*, of which I shall make use, though I shall allow myself some observations on them, gives the name of hyper-oxygenated to these latter combinations, which has the advantage of being entirely drawn from the same language.

Since the oxygenated muriates show no signs of saturation, and since the acid, and particularly the oxygen, experiences successive and indeterminate degrees of condensation in them, the denomination by which they are designated must be received with the uncertainty which is found in the combination itself.

This fluctuation in the constitution of the combinations of oxygenated or super-oxygenated muriatic acid, also prevents the ascertaining the correspondence between the properties of the combinations, and those of their elements, which can be traced in the combinations of the other acids with alkaline bases: in these we are con-

\* Philos. Trans. 1802.

finer to stating the properties of the combinations, to be able to foresee and explain their effects; but they can only be admitted with reserve into the general considerations of acidity and alkalinity.

316. The oxygenated muriatic acid acts with more energy by its elements, that is to say, it is more easily decomposed when it is in the state of gas than when it experiences the action of the water which holds it in solution: thus it supports the inflammation of burning bodies; it inflames metallic substances reduced into fine powder, and ammonia, as has been shown by Westrumb and Fourcroy; liquefied sulphur also inflames in it; it decomposes carburated hydrogen gas (282), either by depriving it of part of its hydrogen, and by that means precipitating the charcoal, or, by giving oxygen to the remainder of the hydrogen combined with the carbon, whence results either the formation of carbonic acid, or that of oxicarburated hydrogen. It does not, at first, act sensibly on hydrogen gas when it is mixed with it, but it appears from the experiments of Cruikshank, that it destroys it by a continued action; the electric spark causes this mixture to detonate, and the effects vary according to the proportions, as when this operation is performed with oxygen gas, so that the result is water, carbonic acid, or oxicarburated hydrogen gas: Cruikshank concluded\*, from the results of this detonation, that a

\* Bibl. Brit. Tom. XVIII.

volume of 2.3 of oxygenated muriatic gas contained 1 of oxygen, supposed in the gaseous state: it cannot precipitate the carbon of the oxo-carburated hydrogen gases, but it gradually completes the combination of carbon and hydrogen, and by that means converts them into carbonic acid and water\*; nevertheless according to the observation of Cruikshank, the electric spark does not cause this mixture to detonate.

When the oxygenated muriatic gas has become liquid by its combination with water, it produces only part of the preceding effects; nevertheless, it still oxides the metals which it can burn; it acts on the olefiant gas, and changes it into a species of oil; but it more particularly retains its energy on the substances with which it can enter into intimate contact: thus, though it cannot then attack sulphur, if the latter acquires the liquid state by its combination with an alkali, or if it is in the state of sulphurated hydrogen, the oxygenated muriatic acid changes it into sulphuric acid: it can only acidify phosphorus by the aid of the action of light.

The substances which are oxygenated by the gas, give light, and sometimes with a report; but with the liquid only heat is produced: this is one of the facts best calculated to prove that the caloric which is disengaged from these combinations can take the state of light, or simply pro-

\* Cruikshank. *Ibid.*—Guyton, Desormes and Clement. *Ann. de Chim. Messidor. An. IX.*

duce heat, according to the circumstances (126). When the oxygenated muriatic acid, either in the state of gas, or in the liquid state, acts on a combination which contains hidrogen, it is this which begins by combining with the oxygen, so that the substance with which it was united, is abandoned, although it may be susceptible of oxigenation itself; and sometimes the force of cohesion which it then acquires withdraws it from the action of the oxygenated muriatic acid, if a sufficient quantity of it is not employed at first.

Thus, when oxygenated muriatic acid is poured by portions into water impregnated with sulphurated hidrogen, or an hidrogenated sulphuret, or a hidro-sulphuret, or an hidrogenated phosphuret, the phosphorus or the sulphur is precipitated, and being stro<sup>ngly</sup> condensed is no more attacked: but there is not any precipitate if the inverse operation is performed. These phenomena are analogous to those obtained when these gases are detonated with a small proportion of oxygen, and also to those which are observed in the combustion of the compound hidrogens according to the quantity of oxygen gas which effects the combustion (282).

Sometimes the oxygenated muriatic acid combines with a substance containing hidrogen without producing or experiencing decomposition, and it is only by a slow action, or by a change of temperature, that the mutual decomposition is effected:

effected : it is thus that this liquid acts on the colouring parts of vegetables ; it causes their disappearance by forming a combination with them free from colour and soluble in the alkalis : but if this combination is long abandoned to itself, or exposed to the temperature of ebullition, it changes its nature ; its hydrogen produces water ; it grows yellow ; it chars, or approaches to charcoal.

316. The action of the oxygenated muriatic acid on the alkaline bases is difficult to elucidate, and more especially to describe, from the variety of combinations which it can form, according to the state of its condensation, and according to the concentration and affinity of the alkaline base : when the action which it experiences is carried to a certain point, its oxygen condenses in one part of the muriatic acid only, by forming a combination whose proportions are determined by the stronger reciprocal affinity of the elements (195, 207), while the greater part of this acid, deprived of oxygen, unites with the remainder of the alkaline base ; but a great quantity of the oxygenated muriatic acid remains in combination without changing its nature : finally, a part of the latter acid is usually decomposed by the action of the alkaline base, and abandons the oxygen which is disengaged in gas. I shall now trace part of the phenomena which are owing to this complex action.



While the oxygenated muriatic acid has only the condensation which it can take when it is dissolved by water, it does not expel the carbonic acid from the carbonates: it even dissolves carbonate of lime, and probably would dissolve the carbonates of magnesia, of barites, and of strontian; it therefore does not form a super-oxygenated muriate, for in that state it very probably would drive off the carbonic acid, and the part which would be reduced into muriatic acid would produce the same effect: by this solution the odour of the oxygenated muriatic acid is almost wholly dissipated, and the liquid loses all its colour.

If carbonate of lime has been dissolved in oxygenated muriatic acid, lime and pot-ash precipitate the carbonate from it; which shows a stronger action on the alkalis than on the carbonates, and which indicates an action similar to that of the acids (259).

If oxygenated muriatic acid gas is passed into a solution of carbonate of pot-ash or of soda, bubbles are soon seen to be disengaged, which are owing to the carbonic acid: then the oxygenated muriatic acid acts on the parts of the liquid which offer themselves to it, it is at once in a state sufficiently condensed to expel the carbonic acid, and a little super-oxygenated muriate seems, at the moment, to be formed.

When the same operation is performed with a solution of pot-ash a little concentrated, and when

when much oxygenated muriatic acid is condensed, a part of this acid is decomposed by the stronger action which the alkali exercises on the acid, whose oxygen it disengages, even in the dark, which proves that all the oxygenated muriatic acid is not divided into muriatic acid and super-oxygenated acid, as soon as it experiences the action of the alkali, although a part may really undergo this change.

Chenevix has doubted the property which I have attributed to alkalis, of disengaging the oxygen gas from oxygenated muriatic acid; he believed that I might have been deceived by a portion of carbonic acid which remained in the pot-ash I employed, which has induced me to repeat the experiment with all the care which the opinion of so skilful a chemist required, and I found that much oxygen gas was really disengaged, and even in the dark: but for this effect to take place it is necessary that there should not be too great an excess of alkali in the combination, and that the oxygenated muriatic acid should have arrived at a sufficiently advanced state of condensation.

The different alkalis produce this disengagement of oxygen gas; I have not, however, observed it with lime, but barites offers it in a particular manner.

Different changes, therefore, are produced when the oxygenated muriatic acid is received into a  
solution

solution of pot-ash, which vary according to the circumstances, and which, consequently, can only be indicated in a general manner: one part of the oxygenated muriatic acid is converted into super-oxygenated, by the accumulation of the oxygen which abandons a corresponding portion of muriatic acid; this last portion is therefore in the state of muriate of pot-ash.

At the same time, a part of the oxygenated muriatic acid condenses without experiencing any other change, by a combination weaker than the preceding, but what depends on the greater condensation; a portion of the pot-ash seems to correspond to this combination, and it is only by a considerable interval of time that the oxygenated muriatic acid undergoes all the change arising from the transfer of the oxygen, as we shall soon see; but at length an equilibrium of forces is established, and a portion of oxygenated muriatic acid resists ulterior decomposition.

317. The super-oxygenated muriate of pot-ash presents a property which cannot be deduced from those found in its elements, and which depends on some unknown relation between pot-ash and oxygen; or, perhaps, the form peculiar to this combination contributes to the effect; it is a greater insolubility than that of the other super-oxygenated muriates.

In conformity with this exposition, I differ with Chenevix on the period in which the super-oxygenated

oxigenated muriate is produced : he is of opinion that the super-oxigenated muriatic acid is formed as soon as the pot-ash enters into combination, so that, according to him, the oxigenated muriatic acid does not remain in this state when it combines with pot-ash, or at least the quantity which remains is so small, that he does not attribute any sensible property to it : the following is the experiment on which he rests his opinion ; he precipitated a solution of pot-ash, saturated with oxigenated muriatic acid, by nitrate of silver ; he evaporated a similar quantity of this solution, and, having dissolved the residue, he precipitated it, and obtained a quantity of muriate of silver equal to the first : as the nitrate of silver is not precipitated by the super-oxigenated muriate of pot-ash, he concludes that all this salt was formed before the evaporation.

The result of the evaporation may be different, according to the accompanying circumstances of it, but, independent of every other consideration, this experiment does not prove that the oxigenated muriatic acid passes at once into combination in the super-oxigenated state ; for if this were so, the liquor formed by receiving oxigenated muriatic acid in an alkaline solution would cease to be capable of destroying colours, or of being decomposed by light, particularly when there is an excess of alkali : now, a liquor of this species which has received a sufficient quantity of oxigenated muriatic acid, retains the property of  
destroying

destroying colours, or of being decomposed by light, much more than the oxygenated muriatic acid itself, which is only condensed by the water, so that much more of it is then found in the state of oxygenated muriatic acid, because it has received a greater condensation.

I prepared a liquor of this description; I put one half of it into the dark, and immediately exposed the other half to the action of light; after having suffered the first to remain fifteen days in the dark, it was also placed in the light: the quantity of oxygen gas disengaged from the first half was, to that from the second, as 16 to 7.

From this I conclude that although a little super-oxygenated muriate of pot-ash may be formed at the commencement of the operation, when the solution of pot-ash has a certain concentration, it is, nevertheless, only when the acid itself has acquired a considerable condensation that the greatest part experiences the change from oxygenated muriatic acid into super-oxygenated muriatic acid; that this change is continued slowly, even when the liquid does not receive any more oxygenated muriatic acid; and, finally, that the proportions of it which undergo this change may be considerably varied by different circumstances.

The proof by nitrate of silver is not to be depended upon, because it may determine the transfer of oxygen by the action which the oxide of silver exercises on the muriatic acid.

To



To ascertain what proportion of oxygen was combined in the oxygenated muriatic acid, I exposed a determinate volume to the action of light\* ; I obtained a quantity of oxygen gas from it ; I afterwards precipitated the muriatic acid which remained in the liquid, and found the quantity of it by the weight of the muriate of silver obtained by means of a solution of a known quantity of this metal : Chenevix is of opinion that the muriate of silver indicates a greater quantity of muriatic acid than that which I have attributed to it : admitting his correction, 100 ponderable parts of muriatic acid would be combined with 15 parts of oxygen. If this experiment was repeated, taking care that all the oxygenated muriatic acid should be destroyed, it seems to me that an indisputable result would be obtained.

The method which Chenevix has preferred appears, on the contrary, to be liable to inconveniences which are difficult to avoid ; he received a quantity of oxygenated muriatic acid into an alkaline solution, which he afterwards evaporated ; and he judged of the proportion of oxygen by that of the super-oxygenated muriate he obtained, supposing that the oxygenated muriatic acid had entirely experienced the change by which the muriate and the super-oxygenated muriate of potash are formed : but a portion of the oxygenated muriatic acid must inevitably have been disen-

\* Mém. de l' Acad. 1735.

gaged in the evaporation to which he subjected the liquid, and another portion must have been decomposed, from whence it arises that he obtained several inches of a gas which he took for the dilated air of the vessels. Nevertheless he found a proportion of oxygen equal to 0.19, and he made that of the super-oxygenated muriate to amount to 16 with 84 of muriate: my experiments gave me a proportion of super-oxygenated muriate rather less; I think, therefore, that he must have recourse to new observations to remove these slight differences.

The proportion of oxygen in the oxygenated muriate of pot-ash is found with less uncertainty: the experiments which I have published, as well as those of Chenevix, fix it at nearly 38 parts in a hundred.

318. Soda has also the property of forming a super-oxygenated muriate, which has been examined by Dolfuss and Gadolin; but as its solubility differs very little from that of the muriate of soda, it is difficult to separate them; Chenevix crystallized it by means of alcohol, by repeating the operation several times, because the muriate of soda has also the property of dissolving in this liquid: this super-oxygenated muriate, according to his observation, crystallizes in cubes, or in rhomboids but little different from cubes; it is in this last form that I have noticed it: a method of obtaining it, which has succeeded with me, is to leave a very concentrated solution exposed for a long

long time to the air: it seems probable that the temperature of congelation would be capable of producing the separation of the two salts, by varying their respective solubility.

Oxygenated muriatic acid also combines with the earthy alkaline bases, and experiences a change with them analogous to that which it is subject to with pot-ash and soda, but with some relative differences in each species.

Lime has a strong action on oxygenated muriatic acid; it condenses a great quantity of it; if this combination is distilled, much oxygenated muriatic acid is disengaged, and there is only a small quantity decomposed towards the end, so that then a little oxygen gas passes over: the residue which should only be brought to desiccation, does not destroy the vegetable colours, but it sparkles on burning coals with much less vivacity than is done by an analogous mixture of oxygenated muriate of pot-ash: it did not detonate by percussion when mixed with sulphur, but if, in this state, it is urged by fire in a retort, it swells up, and much oxygen gas is disengaged, which shows that a considerable proportion of super-oxygenated muriate had really been formed: nevertheless I have lately observed that it sparkled faintly on burning coals: I conjecture that this difference arises from a greater loss of caloric being sustained than in the super-oxygenated muriates of pot-ash and soda; and, in fact, when the oxygenated muriatic acid is received into pot-ash or soda, no sensible disengagement

gagement of heat takes place, but with lime there is a considerable production of heat.

Chenevix not having been able to separate the muriate and super-oxigenated muriate of lime by crystallization, because both are deliquescent, nor by alcohol, employed an ingenious process with all the similar combinations of earthy bases: he digested phosphate of silver in the liquid combinations, which, as he ascertained, decomposes the muriate of lime, because, on the one hand, the phosphoric acid combines with the lime, and on the other, the silver unites to the muriatic acid, two insoluble combinations; the same thing will take place with the muriates of the oxigenated combinations; I shall, however, indulge myself in one observation on this application of the process.

Chenevix has always considered these combinations as simple mixtures of muriates and super-oxigenated muriates, and he submitted them to his proofs, without having subjected them to the action of heat: now in this state there is a great excess of oxigenated muriatic acid, but little condensed, which will produce much uncertainty in the result.

It must be observed, that in applying it to the processes of the arts, all the oxygen which is condensed in the state of super-oxigenated muriate becomes useless, and that only the muriatic acid which retains its character is efficacious; but, in this respect, the alkaline bases produce different effects:

effects: some facilitate the transmutation into super-oxygenated muriatic acid more than others; they condense the oxygenated muriatic acid unequally, without changing its nature; they also take a variable quantity of muriatic acid, restoring the elastic state to a portion of the oxygen; thus barites absorbs a great quantity of oxygenated muriatic acid, but as much oxygen gas is separated from it, only a small proportion of super-oxygenated muriate is formed with this base.

When ammonia enters into contact with oxygenated muriatic gas, one part is decomposed, and the other enters into combination with the muriatic acid, light is disengaged, and a quantity of water is produced, whose formation may be thus rendered sensible, as was shown by Fourcroy. The decomposition of a part of the ammonia also takes place in oxygenated muriatic acid, its azote is disengaged with the appearance of an effervescence; the other part is preserved from decomposition, by its combination with the muriatic acid: then, instead of light, heat only is disengaged.

Van Mons, by means of a very low temperature, formed a combination of ammonia with oxygenated muriatic acid, or a super-oxygenated muriate of ammonia: other chemists have not succeeded in repeating this experiment.

Chenevix produced this combination by decomposing a super-oxygenated muriate with an alkalino-earthly base, by means of carbonate of ammonia, but he was unable to insulate it, and there may remain some doubts as to the state in which these substances



substances were found: the super-oxygenated acid might have kept a portion of the base to form a triple combination which would have been capable of retaining the ammonia.

319. In the super-oxygenated muriate of pot-ash, and of soda, the oxygen seems to retain not only all the caloric which it had in the gaseous state, but it also has properties which might lead to a conjecture that it possesses even a larger quantity: if the first salt is subjected to a rude friction, luminous sparks are emitted, and a little oxygen gas is disengaged: concentrated sulphuric acid causes it to detonate with jets of light; what supports this conjecture, until it has been submitted to the test of the calorimeter, is, that when the super-oxygenated muriates are formed, by combining a great quantity of oxygenated muriatic gas, quickly, with pot-ash or soda, no heat is sensibly disengaged, as I have already observed, and nevertheless the most considerable part of the pot-ash enters into combination with a corresponding proportion of muriatic acid, and would, consequently, produce much heat, if the caloric was not absorbed by the other combination.

On the contrary, a considerable heat is perceived during the formation of super-oxygenated muriate of lime, which seems to establish a difference in the state of the super-oxygenated muriatic acid in the super-oxygenated muriates; but in all of them the oxygen is overpowered by a stronger affinity than in the oxygenated muriatic acid, and in the oxygenated muriates, for, it does not change  
vegetable

vegetable colours ; it is no longer reducible into gas by light, and by a weak heat ; the super-oxigenated acid does not precipitate the nitrates of silver, or of lead ; the super-oxigenated muriates do not yield their oxygen to metallic solutions, when they are mixed together ; these, however, exercise a slow action, by which the resulting affinity is, at length, destroyed.

The constitution of the super-oxigenated muriatic acid is such, that it cannot be separated from a base in which it is condensed, either by heat, or by the action of the other acids, without being decomposed : nevertheless, a part of this acid seems to be disengaged by the action of sulphuric acid, as was observed by Fourcroy and Vauquelin\*, and it then produces a much more energetic effect on bodies easily combustible, than the oxigenated muriatic acid, so that the mixture of these substances with the super-oxigenated muriate of pot-ash, inflames when thrown into this acid.

When the sulphuric acid is concentrated, its action on the super-oxigenated muriate of pot-ash produces a brisk detonation, which was first described by Pelletier ; if a sulphuric acid is used so weak that the operation may be performed by a moderate heat, and without danger, a yellow liquor comes over, in distillation, which destroys vegetable colours, and which has a peculiar odour, analogous with that of the rutilant nitric acid ; at the same time, a considerable quantity of oxygen

\* Mém. de l'Institut. Tom. II.

gas is disengaged. This liquor may be considered as a compound of muriatic acid and oxygenated muriatic acid; and, conformably to the opinion of Chenevix, it contains a portion of super-oxygenated muriatic acid, which has not been decomposed, but there is no constancy in its composition, in which the proportions vary according to the circumstances of the operation.

Nitric acid produces phenomena but little different: with muriatic acid, the super-oxygenated acid seems to be converted wholly, or for the greatest part, into oxygenated muriatic acid.

When the oxygenated muriatic acid acts on the metals, “there is no decomposition of water, no  
“disengagement of hidrogen gas, and consequent-  
“ly no effervescence; thus, iron and zinc, which  
“otherwise have the property of decomposing  
“water without the aid of any other affinity, dis-  
“solve quietly in oxygenated muriatic acid,  
“because this acid yields to them the oxygen  
“which they want, and the result is the same  
“as if the common muriatic acid had been  
“used\*.”

It is therefore metallic muriates, and not super-oxygenated muriates, which are formed by the oxygenated muriatic acid, which has been confirmed by Chenevix, and when they are distinguished by the denomination of oxygenated, this designation is only applicable to the great oxidation of

\* Séances des Ecol. Norm. Tom. IV.

the metal: but Chenevix has made known the true super-oxygenated metallic muriates. I shall make use of his interesting experiments in treating of the metals.

320. The properties offered by the oxygenated muriatic acid must be deduced from its state of combination, or from the action of the oxygen, and from that which it experiences from caloric. It combines with alkaline bases which condense it, but the oxygen is feebly retained by this combination, and readily forms others which are peculiar to it, abandoning the muriatic acid.

The oxygen accumulates with a part of the muriatic acid, in a proportion which is determined by the stronger reciprocal condensation: then it forms super-oxygenated muriates; it experiences a more energetic action from the alkalis; it is more strongly retained in their combination, and offers more resistance to the action of other substances, unless the resulting affinity is destroyed.

When this effect takes place, whether from the action of a very concentrated acid, or from that of heat, either the acid is decomposed by the expansion which arises, and which is increased by the disengagement of caloric, or its oxygen enters at once into combination, producing the effects which accompany a quick and vivid combustion.

Compression also determines the combination of the oxygen with inflammable substances, by producing a closer contact between these substances and it: but, with Fourcroy and Vauquelin, we

must distinguish the effects of detonation from those of inflammation: it is requisite that the disengaged gas should experience a compression, an obstacle to its dilatation, to produce the first; if this obstacle is wanting, it is only inflammation. (*Note XXI*).

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## CHAP. IV.

### *Of Nitro-muriatic Acid.*

321. THE name of nitro-muriatic acid is given to a mixture of nitric acid and muriatic acid, not to designate a particular substance, but a property, fruitful in effects, which belongs to the mixture of these two acids, and which is a consequence of those we have already recognized in the nitric acid, and of the weak tendency which the muriatic acid has to combine with oxygen to form oxygenated muriatic acid.

When, therefore, nitric acid and muriatic acid are mixed, an effervescence quickly takes place, and the liquid becomes coloured: it has been believed that oxygenated muriatic acid was formed in the liquid, by which it has been attempted to explain the new properties of the mixture; but the gas which is disengaged is the oxygenated muriatic acid, and it is nitrous gas formed by the  
cession



cession of the oxygen to a part of the nitric acid which colours the liquid\*: it may be driven off by means of an alkaline base. It is evident, therefore, that the nitric acid, which has a strong tendency to combine with nitrous gas, a tendency which is also possessed in a less degree by the muriatic acid (304), principally determines the formation of nitrous gas, while the oxygen which is separated from it combines with part of the muriatic acid, and exhales: this effect ceases when the nitro-muriatic acid is saturated with nitrous gas; hence if nitric acid already charged with nitrous gas is employed for this mixture, the effect is less, and much less oxygenated muriatic gas is disengaged, the quantity of which corresponds with that of the nitrous gas produced: the nitrous vapour is also immediately condensed by the muriatic acid, and then no oxygenated muriatic acid is formed; when nitric acid free from colour is employed, the deep colour assumed by the nitro-muriatic acid depends only on the nitrous gas which is produced and condensed.

If nitrous gas is mixed with oxygenated muriatic gas over mercury, or over very little water, the nitrous gas can act on the oxygen, weakly retained by the muriatic acid, independently of the water; the oxygenated muriatic acid is destroyed, and the rutilant nitrous vapour succeeds: but if the mixture is made over a sufficient quantity of water,

\* Mém. de l'Acad. 1785.

the nitrous vapour, as well as the muriatic acid, is dissolved in this water; they then form nitro-muriatic acid, without any disengagement of oxygenated muriatic gas, and without its being produced: here, therefore, results are obtained, which are even opposite to the reciprocal action of the different substances, by a single circumstance which is so often neglected, by the change alone in the proportion of the water, whose action intervenes more or less powerfully, according to its quantity.

Humboldt was of opinion that the oxygenated muriatic acid which absorbs the nitrous gas, separated the azote gas from it, which he thought he found mixed in it, in the proportion of 14 in 100: but if this experiment is made with proper care, not more than  $\frac{1}{10}$  of residue will be left\*; which proves that azote gas does not exist, as an insulated substance, in the nitrous gas which is formed by the common methods, and collected without negligence.

322. The preceding observations are sufficient to account for the action of nitro-muriatic acid on the metals, whether it is formed by the simple mixture of nitric acid, and of muriatic acid, or whether salts containing one or the other acid are introduced into the mixture: then a metal acts on the oxygen of the nitric acid to combine with the muriatic acid, without being required to de-

\* Ann. de Chim. Tom. XXXIX.

compose the water to be oxidated, or to find the oxygenated muriatic acid ready formed.

It is not the oxygenated muriatic acid which is produced that contributes to these effects, since it exhales; neither is it the nitrous gas, which is also eliminated by the action of the metal; but it is the concurrence of the action of the metal, of the muriatic acid, and of the oxygen of the nitric acid, which produces the solution, and which forms the distinctive properties of the nitro-muriatic acid.

It has been remarked with truth, that metallic muriates are produced by nitro-muriatic acid; for the affinity of the muriatic acid for the metals, when they are much oxidized, being considerably greater than that of the nitric acid, it is it which should be particularly considered as forming the metallic combination. I do not, however, adopt the conclusion that the nitro-muriates should be banished from the nomenclature; the nitric acid also exercises an action on the metallic salt, it diminishes its disposition to crystallize, and retains its energy in the circumstances in which the nitro-muriates are used; it sometimes produces ammonia during its action on the metal; its action continues to effect changes in the solution for a length of time: the nomenclature announces these differences by the designation of nitro-muriates.

The nitro-muriatic acid exercises a species of action which requires much attention, because it differs

differs essentially, according to the circumstances, and will serve to explain several analogous facts which come under chemical observation.

The reciprocal action of the two acids, at first, produces two new combinations, but it reaches a term of saturation: if the circumstances are changed, particularly the proportion of water, the new combinations may be restored to their primitive state.

An alkaline base, added to nitro-muriatic acid which has acquired a deep colour, combines simply with the two acids, causing them to abandon their nitrous gas: a substance which has a strong action on the oxygen decomposes the nitric acid, which only acts by its elementary affinities; then the muriatic acid has no influence; but if this substance is metallic, the two acids exercise a very different action; the muriatic contributes to the formation of the oxide by a resulting force; the nitric scarcely acts except by its elementary affinities, and it is by means of its destruction that the new metallic combination is formed.

## SECTION III.

*Of Ternary Acids.*

## CHAP. I.

*Of the Acids commonly designated by the denomination of Vegetable Acids.*

323. THE combination of oxygen with carbon and hydrogen has given us oxi-carburated hydrogen gas, whose ruling properties depend on the tendency to combination with a greater proportion of oxygen.

There are a great number of other fixed combinations which are owing to the union of these three elements; those in which the properties of the oxygen predominate, form a numerous class of acids, which, if the attention was alone directed to the relations of composition, might be only considered as a modification of the same acid; but each of them has an existence sufficiently defined by its stability, and by its properties: nevertheless there is a term at which this division must stop.

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As this ternary combination is frequently formed in vegetables, its varieties are distinguished by the name of vegetable acids ; but chemical skill has succeeded in producing the greater number of these acids, by taking the carbon and hydrogen in the state of division and condensation in which it is found in many substances, and mutually transforming them by the action of oxygen, also condensed in a weak combination : the properties of these acids, therefore, independently of their usual origin, may be considered as resembling those of the binary combinations which are also acids, although they have a different origin.

These circumstances have led to a comparison of the acids arising from the combination of oxygen with carbon and hydrogen, with the modifications experienced by the acids according to the proportions of oxygen and azote, or sulphur, or phosphorus, which enter into their composition, and according to the greater or less state of condensation of the oxygen ; but the introduction of a third element, which may itself vary in its condensation, and in its quantity, renders these modifications more numerous and more difficult to determine : besides, we shall see that this supposition of the composition of ternary acids, which is calculated to represent the principles of action which they are possessed of, is not exactly conformable to what observation has taught us on the state of their elements.

In these acids I shall examine the distinctive properties by which they contribute to chemical effects, and I shall endeavour to find in the proportions of their elements, and especially in their peculiar constitutions, the reasons of their characteristic differences, of their production, and of their decomposition.

324. The acids in question are the malic, the tartareous, the citric, the oxalic, the saccho-lactic, the gallic, the acetic, the benzoic, the succinic, to which may be added the camphoric, the suberic, the pyro-tartareous, the pyro-mucous, the pyro-ligneous, the formic, and probably several others which may offer properties a little distinct, from some difference in the proportions, or in the state of the elements : I have already remarked elsewhere that a too refined division of the acid properties is only an indulgence of little advantage to science : it would establish useless distinctions, because they would only serve to indicate properties whose trifling differences should be overlooked, while chemistry retains so large and so fruitful a field to cultivate : but there are several of these acids which require a particular attention on account of their properties, of the light they throw on many chemical phenomena, and of their utility in the arts.

While these acids preserve their constitution, and act by a resulting affinity, each of them must be considered as a simple substance : in this view they differ from each other by their volatility, by  
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their capacity for saturation, and by the property of forming salts more or less soluble, with the different alkaline and metallic bases.

Some therefore are volatile, and can come over in distillation without being decomposed; others cannot support this operation without experiencing decomposition, and must be considered as fixed, since their resulting affinity ceases as soon as the union of their elements is broken: from this disposition are derived the differences dependent on the volatility and on the fixity, either with respect to each other, or when they are compared with other acids which have a different volatility or fixity, and all that has been advanced on the effects of a difference in the elastic dispositions is applicable to them.

With respect to the capacity for saturation, there is a great difference in these acids; in this, the oxalic acid seems to be superior to all the others: nevertheless, we have hitherto so small a number of facts established with sufficient accuracy, that we must only consider our knowledge on this subject as notions which wait for more precise determinations: the citric acid alone has been examined with accuracy by Vauquelin\*, and I shall insert the results of his experiments.

According to the results of Vauquelin, 100 parts of citrate of pot-ash contain 55.55 of acid, and 45.45 of pot-ash; the citrate of soda, 60.7 of

\* Syst. des. Conn. Chim. Tom. VII.

acid, and 39.3 of soda ; the citrate of ammonia 62 of acid, and 38 of ammonia ; (I must observe that soda and ammonia have different relative quantities with all the other acids;) the citrate of barites, equal parts of acid and of barites ; the citrate of lime 37.34 of lime, and 62.66 of acid: according to Proust, the latter citrate is formed nearly of 30 of lime, and 70 of acid\*.

325. The property by which the ternary acids contribute most to chemical phenomena, and which is the most employed, is that of forming soluble or insoluble salts with the different alkaline bases, and of being useful, by the combination of these properties, in producing the separations which are requisite to ascertain the composition of different substances.

In these comparative properties are found the relations I have noticed between the dispositions of substances which combine together (197). The citric acid, and more especially the tartareous and the oxalic acids, which have naturally such a force of cohesion as causes them to crystallize, and which require a greater or less quantity of water to take the liquid state, form insoluble salts with the earthy bases and with the metallic oxides; for which reason an affinity for these bases superior to that of some other acids which, never-

\* Journ. de Phys. Tom. LII.

theless,

theless, have a greater capacity for saturation, has been attributed to them.

It is true, Scheele says that the citric acid does not precipitate the solutions of lead, of mercury, and of silver ; but some of Vauquelin's experiments seem to prove that it forms insoluble salts with several metallic oxides when it does not experience decomposition, and when it is not in excess.

The saccho-lactic acid itself, which seems to have only a very weak acidity, or capacity for saturation, but which has little solubility, forms crystallizable salts with pot-ash and soda, and insoluble salts with lime, magnesia, barites, and doubtless with strontian, and it precipitates these earthy bases from their solutions ; it acts in the same manner with several metallic salts, and even precipitates all of them if they are employed in a neutral state, to avoid the action of an excess of acid.

On the contrary, the acetic acid forms salts more or less soluble with the alkaline bases and with the metallic oxides. The malic acid has intermediate properties.

326. Scheele, with that discernment which characterized him, employed the difference of solubility of the acids, and of their combinations, to separate those found in the vegetable juices, in which several are blended with each other, and with other substances. It would not be unprofitable



able to young chemists to attend to the processes of this excellent model, and to show, by a new example, how the properties of combinations are connected with those of their elements.

To separate the citric acid from the mucilaginous substances with which it is mixed in the juice of lemons, Scheele formed a calcareous citrate which precipitates: he employed the same process to separate the tartareous acid from the acidulous tartrate of pot-ash; but the citrate and tartrate of lime, which are insoluble in water, easily yield to the action of the acids and suffer themselves to be dissolved: this is not the case with sulphate of lime; although it has but little solubility in water, it opposes a more considerable force of cohesion to the action of the acids, and it resists them, unless the acids are powerful and greatly condensed: the difference of solubility is still greater at an elevated temperature such as is employed in this operation.

If, therefore, sulphuric acid is mixed with citrate or tartrate of lime, sulphate of lime, which displaces the salts which were soluble in an excess of acid, forms and separates.

If, instead of precipitating the acidulous tartrate of pot-ash by lime, a carbonate of lime is employed, only that portion of the acid which exceeds the neutral state can eliminate the carbonic acid; so that the tartareous acid is divided between the lime, disengaged from the carbonic acid, to form an insoluble salt with it, and the pot-ash  
which

which forms tartrite of pot-ash. The oxide of lead produced the same effect in Rouelle's experiments\*.

It is to be observed, that in the preparation of citric acid, it is more advantageous that there should be a small excess of sulphuric acid, than that there should be an excess of lime; the first is easily separated from the citric acid by the strong action which it exercises on water, and by the force of crystallization possessed by the citric acid, while, if it retained a little lime, the action of this excess would render it soluble, which would be an obstacle to its crystallization, as we have seen with respect to the salts, which, by their reciprocal action, destroy their property of crystallizing (77).

The malic acid cannot be separated by this means, because it does not form an insoluble salt with the lime, and, as far as appears, only forms a crystallizable salt when the combination has lost part of its acid; but that which it produces with oxide of lead is insoluble. Scheele therefore formed a malate of lead: this malate is in the same situation as the citrate or tartrite of lime; its insolubility does not resist the action of acids; it is therefore decomposed, and the malic acid is separated from it by means of the sulphuric acid, which produces a sulphate insoluble in the acids.

The oxalate of lime has much more force of cohesion than the tartrite or the malate: this diffe-

\* Hilaire Rouelle, Tableau de l'Anal. chim.

rence obliged Scheele to have recourse to another process, when he was desirous of separating the oxalic acid from the alkaline base with which it is found in an acidulous oxalate in some vegetable substances : he was obliged to seek for an oxalate which could yield its base to another acid, proper to form a more insoluble combination with it : the oxalate of barites offers this property ; its insolubility is less than that of the oxalate of lime, for lime produces a precipitate in water which has stood over oxalate of barites ; it can also form an acidulous oxalate which crystallizes, but which can be decomposed by water like the acidulous sulphates (203) : in the neutral and solid state, oxalate of barites yields to the action of acids with more ease than the oxalate of lime : after having formed the oxalate of barites, it may, therefore, be decomposed by sulphuric acid, this produces a sulphate with the base, which, on the contrary, has a much greater force of cohesion than the sulphate of lime.

It is true that the oxalate of lime can be dissolved by an acid, whence it arises that some chemists having considered the oxalic acid as very proper to detect the lime held in solution by an acid, others have observed that it was only a deceitful index : but the uncertainty may be removed by saturating the acidity with ammonia, as is noticed by Darracq\* ; because the excess of

\* Ann. de Chim. Tom. XL.

the acid is no longer opposed to the insolubility, which then has only the action of the water to contend with.

Nevertheless, the force of cohesion of the oxalate of lime seems too considerable, compared with that of sulphate of lime, for it to be decomposed by the sulphuric acid, as can be done with the malate and tartrite of lime, or at least the process would only give an incomplete and much more unprofitable decomposition.

The sulphate of lead has the same properties with respect to the oxalate of lead, as the sulphate of barites compared with the oxalate of barites. There are therefore two methods of separating the oxalic acid from its alkaline bases, and other similar ones may be found. The oxalic acid, thus disengaged from its base, does not differ from the acid which was known under the name of acid of sugar.

From the force of cohesion which is peculiar to them, the oxalic and tartareous acids have the property of forming insoluble combinations (199) with the bases which have little solubility, and, with the others, acidulous salts which have much less solubility than the neutral combinations with the same bases: in this case the acid produces an effect analogous to that by which the alkalis which have solubility precipitates the bases which are deprived of it, by diminishing the action exercised on them by an acid, by which it overpowered the effect of their force of cohesion (65).

The

The oxalic and tartareous acids therefore form salts with pot-ash, soda, and ammonia, which are much less soluble in the acidulous state than when they are in the neutral state; but the tartareous acid possesses this property in a higher degree than oxalic acid: according to Bergman the acidulous tartrite of pot-ash requires 150 parts of water to dissolve it, while the acidulous oxalate of pot-ash requires much less, and shows a much smaller difference between its solubility and that of the oxalate of pot-ash.

The acidulous tartrite of pot-ash tends therefore by its force of cohesion to separate from all the combinations in which it had acquired a greater solubility, and it has a tendency to form, in every circumstance in which the elements which compose it are present, and in a liquid state: in this property are found, 1st, the cause of the partial decomposition of tartrite of pot-ash by a very weak acid, such as the acetic acid, which by its action on an alkaline base sufficiently weakens the force by which this base opposed the separation of the acidulous tartrite of pot-ash; 2d, that of the partial decomposition of the sulphate, nitrate, or muriate of pot-ash by the tartareous acid, which produces a precipitate of acidulous tartrite of pot-ash in the solutions of these salts, from which it carries off a portion of alkali.

Soda forms a much more soluble acidule with the tartareous acid than the acidulous tartrite of pot-ash; hence it arises that the tartareous acid



does not produce a precipitate in salts with base of soda; it is, however, very probable that if the experiment was made with much less water there would be also a precipitate: but the ammonia having the same property as the pot-ash, the tartareous acid abstracts a part of the base from ammoniacal salts, to form the acidulous tartrite of ammonia.

Although the acidulous oxalate of pot-ash has less insolubility than the acidulous tartrite of pot-ash, the oxalic acid has also, according to the observation of Scheele, the property of decomposing the nitrate of pot-ash, and also all the neutral salts with base of pot-ash and of soda; but to obtain this decomposition, the saline solutions, and those of the oxalic acid must be employed in a state of concentration.

327. The properties I have now examined belong to the ternary acids from the instant of their formation to their decomposition; they are derived from the resulting affinity by which they tend to combine like a simple substance; from the greater or less disposition to take the solid state, which combines with that of the bases associated with them; and from the condensation which is owing to the combination. The effects of this condensation differ according to the capacity for saturation; they may also receive some variations from the figure which is determined (213), or from some other condition which escapes notice; so that although the phenomena permit the principal  
action

action of the causes which I have just pointed out to be perceived, the properties of each combination must be ascertained by experiment, more especially as we have just seen that a small difference in the solubility by water, or by the acids, or in the force of cohesion, may become efficacious in determining the combinations by which different substances are separated, and a knowledge attained of those which belong to a compound, or are found in a mixture.

From these absolute notions, let us proceed to those which may be formed on the composition and decomposition of these acids. I have supposed them, with Lavoisier, as formed of oxygen, of hydrogen, and of carbon, because this supposition is sufficient to form a clear idea of their general properties; nevertheless azote enters into the composition of the tartareous acid, according to the observation of Hassenfratz, and it probably contributes to its distinctive properties; in fact, when the acidulous tartrate of pot-ash is calcined by a sufficient heat, the residue forms a little Prussiate of iron with the solutions of that metal, and when it is distilled, the liquid acid found in the receiver contains a little ammonia\*: but as the influence which the azote may have on the properties of this acid is not perceived, I shall neglect this element here.

If the attention is directed to the circumstances of the formation and decomposition of the ternary

\* Tableau de l'Anal. Chim.

acids, it is not enough to consider them as combinations of three elements which only vary in their proportions; but they must be considered as combinations of oxygen with a compound substance, in which the elements are more intimately united, so that they have all one base which differs in its proportions, and its condensation; thus water, which is a combination of condensed oxygen and hydrogen, unites with oxygen gas, or oxygen gas dissolves in water, without this union being considered as owing to these elements united in the same state of condensation, and exercising a chemical action which is only determined by the nature of each substance.

It seems therefore that, in the greater part of the ternary acids, a substance composed of carbon, oxygen, and hydrogen, acts by a resulting force on the oxygen, and becomes acid by being surcompounded with it; this base seems to differ in these acids, either by the proportions of the elements which compose it, or by the constitution which they preserve in it: but on this subject only conjectures can be formed.

When nitric acid acts on a vegetable substance, the first acid formed is the malic: this acid is easily decomposed by heat, and leaves a voluminous light coal, similar to that obtained from saccharine substances\*; it also readily experiences a spontaneous decomposition. When the oxygenated mu-

\* Syst. des Conn. Chim.

riatic acid acts on vegetable substances, it can only exercise a weak action considering its state of dilatation, and by this means, only malic acid is formed; by an action rather stronger, the nitric acid produces oxalic acid, and it is probable that part of the malic acid which was first formed, acquires by this means the character of oxalic acid: this does not experience spontaneous decomposition; it offers more resistance to its decomposition by fire, and scarcely leaves any charcoal, but is reduced into a liquid acid, which seems to approach the acetic acid, into carbonic acid gas, and oxi-carburated hydrogen gas.

From these observations it may be concluded that the oxygen is more abundant, and more condensed in the oxalic acid than in the malic; that the latter partly retains the properties of a vegetable substance; and, that, in respect of its composition, it should rather be considered as this substance acidified, or serving as a base to the oxygen, than as an acid resulting from the new union of its three elements; the stronger action of the nitric acid finishes by destroying the combination which the vegetable substance formed, and the oxalic acid, much more powerful, and more durable, succeeds the malic acid; so that of these two ternary acids, the oxalic seems to be that whose base retains the least of a peculiar existence.

Some substances, besides the malic and oxalic acids, yield that which has been named saccho-lactic,

lactic, because Scheele obtained it at first from sugar of milk, and the differences of composition which distinguish it are not yet known.

To this name Fourcroy has substituted that of mucous acid: I do not think it right to adopt this denomination; 1st, because it is not an exclusive property of the mucus to be capable of forming it: the sugar of milk is evidently a saccharine substance; 2d, because all mucus does not produce it; gum Arabic does not yield any, while a great quantity of it is obtained from gum tragacanth; 3d, because the termination in *ous*, as has been observed by Chenevix, supposes the property of undergoing a change analogous to that experienced by the sulphureous and phosphoreous acids when they pass to the state of sulphuric and phosphoric acids; which does not happen with any of those which I have designated as ternary acids. It is therefore with an inconvenience in the nomenclature which I do not disavow, and which perhaps ought to be rectified, that I retain the denomination of tartareous acid.

328. The citric and tartareous acids seem to me to have relations to each other similar to those I have pointed out between the malic and oxalic acids. The citric acid has not yet been produced by means of the nitric acid, and Scheele, by submitting it to the action of the latter acid, was unable to form oxalic acid: Fourcroy and Vauquelin succeeded in obtaining a small quantity from it, but it was by employing much nitric acid: there



there is yet only one very doubtful observation on the formation of tartareous acid by nitric acid: the production of oxalic acid, by its intermedium, seems also either very difficult, or impossible.

The tartareous acid decomposes spontaneously in the state of acidulous tartrite of pot-ash\*, and leaves the pot-ash in the state of a carbonate, united with a considerable quantity of oil: it is easily destroyed by the action of heat, yielding a little acid of another character, much oil, carbonic acid, and oxi-carburated hydrogen gas, and it leaves a voluminous coal.

The citric acid resists its decomposition much more, and leaves much less coal: Fourcroy, who has given the analysis of it, makes no mention of oil; perhaps it is destroyed by the strong heat necessary to decompose this acid; perhaps it might be obtained by decomposing a citrate; but that which induces me to suppose that it enters into the composition of this acid as well as into that of the tartareous acid, is, that I find, in this supposition, a reason why the nitric acid, which acts particularly on the hydrogen of vegetable substances, can neither produce this, nor the tartareous acid: besides, I observe that one of these acids easily takes the nature of the other by vegetation; thus Scheele observed that, before maturity, grapes contained only citric acid, and Rouelle, as well as several chemists since him, ob-

\* Mém. de l'Acad. des Sciences, 1782.

tained acidulous tartrite of pot-ash, from the juice of ripe grapes : it is notorious that a considerable quantity is deposited in the vessels which contain the wine. I conjecture, therefore, that these two analogous acids must have an oily substance for a base, whose proportion is greater in the tartareous than in the citric acid.

329. The acetic acid is distinguished from the preceding by a much weaker disposition to assume the solid state, and by a greater volatility; so that, with the alkaline bases and with the oxides, it forms much more soluble salts; and, by its elasticity, comes over in distillation, without experiencing decomposition: hence also, when it is submitted to the action of heat, it gives the place it occupied in combinations, to the acids which are more fixed, independently of the capacity for saturation (155).

Priestley observed that the acetic acid could take the form of a permanent gas, which he called *vegetable acid air*: but water absorbs it with facility, and the acetic acid may be considered as a solution of this gas in water, whose specific gravity it augments but little. When this acid is much diluted with water, it may be separated by congelation, but only to a certain point, for it terminates by congealing with it; so that its concentration is limited by this circumstance, and it cannot be brought to a term which it could attain by other means.

If the elastic disposition of acetic acid, and the weakness of its acidity are considered, it will appear very probable that its distinctive properties depend on the state of dilatation in which the oxygen and hydrogen are found in its composition.

This conjecture is also supported by the circumstances of its formation; it is almost always by the absorption of oxygen gas from the atmosphere that it is produced, and this gas, opposing a resistance to its fixation, retains a part of its elasticity, as we have seen that that which was absorbed by the hydro-sulphurets formed sulphureous acid at first (290).

If it is produced by treating vegetable substances and alcohol with nitric acid and oxygenated muriatic acid, it may arise from the oxygen which existed in these substances, although they were without acidity: when distillation is employed, the dilatation experienced by the elementary parts may decide the formation of the acetic acid. There is not even a necessity for distillation to produce this effect; it is enough that an acid exercises a powerful action on a vegetable substance, for this combination to be produced by the association which its elements tend to form, by means of the heat which accompanies this action; thus the sulphuric acid determines the formation of acetic acid by its action on several vegetable substances, as was observed by Fourcroy.

In fact, the other ternary acids are changed by distillation into the acetic acid, or an acid analogous

gous to it, such as the pyromucous, the pyrotartareous, the pyroligneous, which differ so little from the acetic acid, that it is expedient to blend them in the chemical system, as has been proved by Fourcroy and Vauquelin: in this change a part of the base which forms these acids is retained by its fixity, and that which afterwards constitutes the acetic acid will receive the degree of expansion which puts it in a state to support the distillation; but this consideration should render us cautious on the indications drawn from the products of distillation: it does not follow because acetic acid or some analogous acid is obtained by it, that it existed ready formed in the substance from which it is procured: so, when a compound acid is rectified by distillation, and the properties of acetic acid are found in what passes into the receiver, it must not be concluded, without precaution, that this was the nature of the acid before distillation.

The same chemists have also shown, lately, that the formic acid is only a mixture of the acetic and malic acids\*.

The other ternary acids may not only be changed into acetic acid when they abandon part of their charcoal by the action of heat, and when their elements, which least resist this action, separate by being volatilized; but the same change may take place by the action of a metallic oxide; thus when oxalic acid is treated with highly oxidized

\* Bulletin de la Soc. Philom.

manganese, it experiences a decomposition in which carbonic acid and acetic acid are formed; the latter then combines with the manganese, and restores it to that state of oxidation which is suitable to its combination with this species of acid. Similar transmutations of ternary acids by metallic oxides, will doubtless be effected on many occasions: hitherto they have been little attended to, but they should not be lost sight of when the mutual action of these substances is examined.

If the acetic acid is not decomposed by heat when it is free, this is not the case when it is retained by a base; then it supports a more considerable degree of heat, without being volatilized, and the most volatile of its principles separate and form more elastic combinations, carbonic acid, and an inflammable gas which appears to be carburated hydrogen (*Note XX*), while a part of the charcoal is insulated, and forms a residue: the effects of this decomposition vary according to the energy of the base, and according to its nature, particularly if it is an oxide which contributes to it by the intervention of its oxygen; thus with acetite of lead, an inflammable liquor is obtained whose properties are little known\*.

The expansion which I suppose in the elements of the acetic acid, and the weak union of its elements explain the spontaneous decomposition of acetite of pot-ash, which is much more easy than

\* Rouelle, *Tableau de l' Anal. Chim.*



that of the tartrite, and which, in its result, yields an alkali changed into a carbonate, and united with a small quantity of a substance which has an oily appearance\*.

When the acetate of copper is submitted to distillation, the water is vaporized, and abandons this salt before the acid separates or is decomposed: after this, one part of the acid is decomposed and reduces the oxide, while another part passes in the distillation in a great state of condensation; this is what has been designated by the name of *radical vinegar*.

330. Deceived by some appearances†, I was of opinion that the acid obtained from the distillation of the acetate of copper, had properties which distinguished it from the common acid: on this foundation it was thought necessary to distinguish the acetic acid from the acetous, considering the first as owing to a greater proportion of oxygen, and as analogous to the sulphuric and phosphoric acids, compared with the sulphureous and phosphoreous acids: it was an exuberance of a new and copious theory.

Adet examined this subject with more care: he has shown, 1st, that when the acetate of copper is distilled, the oxygen lost by the oxide is only employed in the production of the carbonic acid; a very small quantity either serves for the for-

\* Mém de l' Acad. 1782.

† *Ibid.* 1783.

mation of water, or rather enters into the composition of the oxi-carburated hidrogen, which is found with the carbonic acid; 2d, that the acid obtained by distilling acetate of copper, offers no real difference from the acetous acid, and that it forms combinations with the alkaline bases which do not differ essentially; 3d, that by oxygenating the acid considered as acetous, by means of the oxygenated muriatic acid, it is destroyed, instead of acquiring the properties attributed to the acetic acid; 4th, that with the metals, the two acids formed combinations exactly similar: he concluded that probably their difference depended only on the quantity of water, which is much greater in the acetous acid than in the acetic. Nevertheless, Adet observed some difference between the combinations of the two acids with pot-ash and soda, and Chaptal has shown that, in some circumstances, the acetous gave traces of a greater quantity of charcoal than the acetic, particularly when they were treated with sulphuric acid \*.

At length Darracq dissipated all the obscurity which might remain on this subject †; he has confirmed the greatest part of the results which Adet had published, and has shown, by many comparative experiments, that both acids produced the same combinations, and gave the

\* Ann. de Chim. Tom. XXVII.

† Ibid. Tom. XLI.

same products in their decomposition; that the only difference consisted in a little mucilaginous substance which separates when the acid, which had been considered as acetous, enters into combination, and in a greater proportion of water; he brought it to the state of acetic acid by distilling it several times over muriate of lime, which, at each operation retained part of the water, and then he was able to form ether with this acid and alcohol, as with the acetic acid obtained from acetate of copper. It is therefore indubitable that the acetous acid must not be longer distinguished from the acetic, and that only the latter should be retained in the nomenclature.

It is therefore the affinity of the acetic acid for water, and the slight difference in their volatility, which hinders it from being sufficiently deprived of this liquid to attain the point of condensation which it has when it is obtained from the acetate of copper: congelation is not capable of separating this water, because, as I have already remarked, the acetic acid itself congeals with it, when the temperature is reduced to the point which is requisite to separate the water completely.

Westendorf has given a method of procuring the acetic acid in a very advanced degree of concentration, by distilling the acetate of pot-ash with half its weight of sulphuric acid; Lowitz has improved the process, by means of which he obtained the highest degree of concentration; for this

this purpose, he distilled three parts of acetate of pot-ash with four parts of sulphuric acid; the excess of the sulphuric acid retained the water which the acetate of pot-ash had held, and which would have passed with the acetic acid in the distillation; he distilled the acid obtained in the first distillation, a second time, with acetate of barites, which retained the sulphuric acid that might be in it, and after this the acetic acid was so condensed that it was reduced into crystals\*.

Two other volatile acids, the benzoic and the succinic, seem to have a resin, or rather a volatile oil for a base, so that they are easily inflammable; their acidity is so weak, that it is difficult to determine the properties of their combinations, and that we have but an imperfect, and even contradictory knowledge of them; thus the benzoate of lime is considered as possessing a tolerably great solubility, and nevertheless it is said that lime water forms a precipitate with the benzoate of pot-ash, without the cause of this difference being determined.

The composition of the benzoic acid is deserving of particular attention, not only because it exists in several resinous substances, but particularly because it is found in the urine of infants, according to the observation of Scheele; and in that of all the herbivorous animals, and in dunghill-waters, according to those of Fourcroy and Vauquelin.

\* Journ. de Van Mons, No. IV.

With respect to the composition of the ternary acids, I have indulged myself in conjectures which should not be confounded with the consequences which I have drawn from the distinguishing properties of these acids, and which are ascertained by experiment.

From these last considerations, I have deduced the properties of the combinations which they form, and especially those which depend on the force of cohesion belonging either to the acid, or to the base with which it unites, and which is increased by the condensation produced by the combination.

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## CHAP. II.

### *Of the Prussic Acid.*

331. THE ternary acids which I have considered in the preceding chapter, have a constitution which is but little liable to vary, so that they retain properties in their combinations which may always be compared with each other, and which are always analogous to those of other acids which act by a direct, or by a resulting affinity, while they



they do not experience decomposition: it is not so with the Prussic acid; its constitution experiences great variations which modify its properties considerably. In this respect it may be compared with the oxygenated muriatic acid, with this difference that it is much further removed from the acids, and that it does not, in reality, take this character except when it is sur-compounded.

The Prussic acid at first only engaged the attention of chemists by the properties of prussiate of iron, the discovery of which was owing to chance: Macquer learnt to combine the peculiar principle of it with the alkalis, and to cause it to pass, by their means, into other combinations; but only idle conjectures were formed on its formation, and on its distinctive properties: it is to Scheele that we are indebted for the means of insulating it; for the knowledge of the chemical qualities it possesses in this state; and for that of the greater part of the combinations it can form.

Since the properties of the Prussic acid discovered by Scheele, and those which have been since recognized, seem to me to have been passed over in an incomplete manner in the chemical treatises; since even lately, ideas have been formed of these combinations which appear to me to be inaccurate, I shall examine them with some particularity. I am the more induced to this by its importance in the arts, and in the analysis of animal substances, from which it is produced.

Scheele, having mixed an acid with the prussiate of pot-ash and iron, for which we are indebted to Macquer, and which I shall only designate by the name of prussiate of pot-ash, observed that on submitting the mixture to distillation, a liquid passed which contained the colouring principle, and that during this operation, prussiate of iron remained in the retort: this liquid does not change the vegetable colours; when it is combined with the alkalis, it does not neutralize them in the manner of the acids; all the acids disengage it from this weak combination, and the carbonic acid which is found in the atmospheric air is sufficient to produce this effect; it appears also that the dissolving action of the atmospheric air can disengage it, for the alkalis do not entirely suppress its odour: if, therefore, an acid is poured on this combination, the substance which is called Prussic acid is disengaged by taking the elastic state, and the liquid no longer forms a blue precipitate with solutions of iron, or only yields a small quantity: if the liquid containing the Prussic acid and pot-ash is boiled with oxide of iron, or if a little solution of iron is added to it, the oxide enters into combination with the Prussic acid, and gives it new properties; another acid no longer drives it from its combination, unless heat is employed, or the mixture is exposed to the light.

It is in this state that the Prussic acid passes in combination with an alkali, of any kind, when it is

is made to act on prussiate of iron : pot-ash and soda saturated with Prussic acid, and with a suitable portion of oxide of iron, crystallize : the prussiate of pot-ash obtained in this manner forms yellow crystals of an octahedral figure, of which two opposite pyramids are truncated at their base, from whence result square plates whose edges are bevelled.

The solution of these crystals does not change the blue or yellow papers : the Prussic acid, which, without the oxide of iron, offered only the weak acid property of precipitating sulphurets, and disturbing the solution of soap, has therefore taken, by means of the oxide of iron, a much more powerful character of acidity ; nevertheless it has still particular properties which distinguish it, and which more especially depend upon its strong action on some oxides.

332. When an alkali acts on prussiate of iron, it will require a great quantity of it to be capable of carrying off all its Prussic acid ; it only makes a division ; the oxide of iron retains a variable proportion of Prussic acid, according to the power of the alkali, and then forms another prussiate, of a yellow colour, bordering more or less on red, and which, to distinguish it from the blue prussiate, may be called prussiate with excess of iron : but this yellow prussiate may have very variable proportions of the elements which compose it\*.

\* Mém. de l'Acad. 1787.

If an acid is poured over this prussiate a new division is made, but it is the oxide of iron which is the object of it: the new acid takes one portion, and leaves the other in the state of blue prussiate, which may afterwards be brought to the state of yellow prussiate by the action of an alkali: by these successive opposite actions the decomposition of the blue prussiate is accomplished.

In exercising this action on the blue prussiate, the alkali dissolves an excess of oxide of iron: hence it arises that if an acid is poured into it, a blue precipitate is instantly formed. As these alkaline prussiates are used to discover the presence of iron, different methods have been sought of separating the oxide of iron, which was supposed to be wholly foreign to the alkaline prussiate; but that which is essential to this prussiate, and which is not precipitated by the acids, must be distinguished from that which is in excess, and which from being precipitated by the acids, may lead to an error on the existence of iron which it is wished to discover in a substance: the method which appears to me to be the most simple consists in lightly calcining, or rather roasting, the prussiate of pot-ash obtained by a first crystallization, and afterwards proceeding to a second crystallization: the crystals obtained in this manner may be considered as constant in their composition. Scöpoli advised the exposure of a mixture of prussiate of pot-ash, and an acid, to the solar rays; but by this means the prussiate of pot-ash is entirely decomposed;

composed ; here the light acts, as the heat does at the degree of ebullition (127) ; the prussiate of iron is precipitated, and the surplus of the Prussic acid exhales ; but it must not be overlooked that when heat is employed, or the mixture which has been made is exposed to the light, the best prepared alkaline prussiate abandons blue prussiate, which may easily lead to error.

In the method of purification which I have recommended, a yellow precipitate is made, and a similar precipitate is formed when solutions of unpurified alkaline prussiates are kept ; it is a prussiate with excess of oxide, which may be also brought to blue by means of an acid.

The carbonates have also the property of taking the Prussic acid from the blue prussiate ; Bergman noticed this in carbonate of lime, and Fourcroy in the carbonates of magnesia and barites ; but when successive operations are made, it happens in the last of them that the oxide of iron which is the base of the residue, retains all the carbonic acid, and the prussiate which is formed does not contain any.

It is supposed that when a solution of iron is precipitated by the prussiate of an alkali, an exact change is made, that the alkali combines with the acid, while the Prussic acid passes into combination with the oxide of iron ; but this is not what takes place : although the alkali may be in a much greater quantity than is requisite for saturating the acid of sulphate of iron, for example, the super-natant liquid retains sulphuric acid in excess ;



excess ; the first washings also give indications of acidity, and when these indications cease, the liquid, on the contrary, contains a prussiate of the alkali, which gives a blue precipitate when an acid is mixed with it : a liquid entirely deprived of prussiate of alkali, can hardly be obtained by a great number of washings.

Hence it follows that the prussiate of iron takes a considerable quantity of prussiate of alkali which does not contribute to its colour, or only modifies it : this explains the great weight of prussiate of iron precipitated from a solution of this metal, by means of prussiate of pot-ash, compared with that of the oxide which enters into its composition. Bergman observed that the Prussic acid, contained in 128 parts of Prussian blue, was capable of saturating nearly 218 of pot-ash ; now, this quantity of pot-ash is very superior to that which is necessary to saturate the acid of the sulphate of iron which could form these 128 parts of prussiate of iron.

333. What precedes shows that the Prussic acid, by itself, has only so weak an action on the alkalis, that it ought not to be classed among the acids ; that by the addition of the oxide of iron (and other oxides can produce the same effect) it acquires much more analogy with the acids ; that in this state it can form variable combinations with the alkalis, but that they may be brought to a uniform state, in which the acids do not act on their composition, unless heat and light are employed ; that when these prussiates decompose metallic solutions,

solutions, it is not a simple exchange of base which is made, but part of the alkali enters into the insoluble combination.

With respect to the combination of the Prussic acid with the oxide of iron, it is obvious that, according to the state of the forces which act, it can be formed in different proportions, which cause a variation in its colour and in its properties ; but that it may be vaguely distinguished into blue prussiate and yellow prussiate.

334. A celebrated chemist, Proust, has offered an opinion on the state of oxidation of the iron which forms Prussian blue, which has been adopted, but which, however, does not appear to me to be founded : Proust considers only two degrees of oxidation as possible in the solutions of iron, that of the greatest, and that of the least oxidation. With the sulphate in which the iron is least oxidized, the Prussic acid forms a white prussiate, and this only passes into the blue state when its metal takes the most oxidized state by means of the oxygen which it attracts powerfully from the atmosphere\*.

I made a mixture of prussiate of pot-ash and of the least oxidized sulphate of iron ; I observed that the sulphate of iron retained its taste, though it was mixed with a considerable proportion of prussiate of pot-ash ; I added to it a certain quantity of distilled water, and immediately the mixture

\* Journ. de Phys. Tom. XLIX.

became

became of a deep blue with a greenish tinge; a little muriatic acid gave it a blue colour, without a possibility of suspecting any sensible action from the atmospheric air, considering the rapidity of the successive operations.

I formed white prussiate in a glass, and conveyed sulphuric acid to the bottom of the vessel; all the lower part which the sulphuric acid could reach became of a beautiful blue, while the upper part retained its whiteness: nevertheless, I find a contrary assertion in Proust's memoir; it is said there, *the sulphuric and muriatic acids, poured into the white prussiate of iron, do not occasion any change in it*: experiment must decide between us.

I put some white prussiate into a small flask, which I filled with muriatic acid, and corked it instantly; it became perfectly blue: the experiment had the same success with sulphureous and with phosphoreous acids.

It will, no doubt, appear clear to those who repeat these easy experiments, that it is not necessary that the iron should be at the highest degree of oxidation to form a blue prussiate: but the formation and difference of that which is called the white prussiate must be explained.

In treating the metallic solutions, we find that the oxide of iron tends much more strongly to the sulphuric acid when it is little oxidized than when it is much so; therefore the sulphate of iron which is but little oxidized is not decomposed by prussiate  
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of pot-ash ; nevertheless, these two substances exercise a mutual action which separates them from the small quantity of water which they contain ; but if this quantity is sufficiently augmented, the action of the sulphuric acid is so weakened that the combination of the oxide of iron with the Prussic acid can be formed : the oxide of iron in this combination is also in too great a proportion, which is the cause of the greenish tinge, which disappears by the action of an acid. It must also be remarked that a very oxidized sulphate of iron acts by the excess of acid which it necessarily has.

When an acid is poured on a white prussiate it tends to combine with the alkali, and thus the action of the Prussic acid on the oxide of iron is augmented : the sulphureous and phosphoreous acids which tend to take oxygen, and the muriatic acid which cannot yield any, produce this effect, as well as the acids which yield their oxygen with facility.

If the white substance is left in contact with the air, the sulphate, by becoming oxidized to a higher degree, loses the property of forming a white prussiate immediately ; so that the real difference which exists between the sulphates, in this respect, consists in that which is little oxidized being unable to form a blue prussiate unless it is diluted with a certain quantity of water, but with this single condition they can all produce it.

There is nevertheless some difference between the blue prussiates according to the state of oxidation :

dation : that in which the iron is little oxidized has a clearer blue, and precipitates much less readily from the liquid ; kept in the air in a humid state, it attracts oxygen from it, and oxidizes more and more ; but I do not know whether it acquires the same degree of oxidation as that which is immediately formed by a very oxidized sulphate, or whether the oxidation stops at a certain term.

335. We have just seen that the Prussic acid, in the common prussiate of pot-ash, owes the greatest part of its energy to the oxide of iron : this strong action of the Prussic acid on the oxides is not confined to the oxide of iron ; but it is very unequal in respect of the different oxides, so that, as yet, no general principle can be established on this subject.

The Prussic acid exercises so strong an action on the oxide of mercury, that the oxygenated muriate of mercury decomposes the prussiate of iron, and causes the colour to disappear : the circumstances of this decomposition, observed by Scheele, are not yet known.

The red oxide of mercury decomposes the prussiate of iron with ease, and forms a soluble combination with the Prussic acid, from which prismatic tetrahedral crystals are obtained. This combination is not decomposed either by lime, by pot-ash and soda, or by muriatic acid, but is so by the action of sulphuric acid on the iron ; this, instead of decomposing water, takes the oxygen from the mercury, and then the Prussic acid, set at liberty,



liberty, passes in distillation, and carries with it a little sulphuric acid; to deprive it of this, the liquid is submitted to a second distillation, adding to it a little alkali, which retains the sulphuric acid. Scheele found this the best method of obtaining the Prussic acid pure, because with the common prussiate of pot-ash, a great part of this acid is retained by the oxide of iron, which thus forms blue prussiate.

With this pure acid, or with its combination with lime, Scheele made different experiments on the metallic oxides and solutions, which prove that it exercises a much stronger action on some of these oxides than the most powerful acids, but they require new elucidations: I shall confine myself to relating some of his results.

The oxides on which the Prussic acid showed the most action are those of mercury, iron, gold, silver, and copper; the solution which it makes of the oxide of silver is not precipitated either by muriate of ammonia, or by muriatic acid. The precipitate which it forms in sulphate of copper is dissolved in ammonia without changing its colour, it can itself dissolve the precipitate which it gives at first, and this also takes place with silver: it precipitates gold, white, but when it is added in excess the precipitate is redissolved; this solution is as colourless as water; the precipitate is insoluble in the acids.

The Prussic acid has a great disposition to form complex salts, as I have noticed in the prussiate  
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of iron, which retains much of the alkali ; thus muriatic acid disengages a portion of the Prussic acid from prussiate of mercury, and the residue crystallizes in needles ; this combination yields a white precipitate with the alkalis and lime-water. By mixing prussiate of pot-ash with a solution of nitrate of barites, crystals were formed which seemed to me to be composed of two salts, which, of consequence, must be a less soluble salt than its components : if the solution of barites is diluted with water to a certain point, no precipitate is formed ; I also obtained a precipitate with sulphate of alumine, and Chenevix made use of the property of precipitating alumine\*, possessed by the alkaline prussiates ; but the composition of this precipitate requires examination, to form conclusions on the quantity of alumine found in it, and which it can indicate by its weight.

Henry has made some experiments which seem to prove that when barites, or a solution of barites in an acid, is mixed with an alkaline prussiate, prussiate of barites is gradually formed which precipitates : it must, however, be better ascertained that it is not a compound salt which is precipitated, as I believe it to be.

He concluded from his experiments that the Prussic acid has more affinity for barites than for pot-ash ; that the barites precipitates with the acid which it takes from the alkaline prussiate by

\* Philos. Trans. 1802.

double decomposition; and, that this character approximates it to the metallic substances, as has been thought by many chemists.

Guyton has shown that this exchange of base is not a proof of a metallic character, and explained it by a preponderance of divellent affinities\*.

In these different cases, the Prussic acid, holding oxide of iron, seems to me to comport itself like the other acids whose least soluble combinations are formed and separate, according to the state of the substances which exercise the chemical action.

The prussiate of barites, being less soluble than the others, deprives them, therefore, of their Prussic acid, at least to a certain point, particularly when the substances are in the neutral state; but this effect corresponds with its insolubility which is not absolute; so that with a certain quantity of water, the precipitation does not take place.

When the Prussic acid has formed a triple combination with an earthy base and carbonic acid, a new quantity of the base forms a precipitate which is a carbonate; and if carbonate of pot-ash is added to a solution of prussiate of barites, as was done by Henry, carbonate of barites precipitates, and prussiate of pot-ash remains, which could be afterwards decomposed by the barites: but in all its effects, the disposition of the Prussic acid to

\* Ann. de Chim. Tom. XLIII.

form complex combinations must not be lost sight of.

336. If oxygenated muriatic acid is mixed with Prussic acid, the first resumes the state of muriatic acid, and the second acquires a much more powerful smell, and seems to have become more volatile: it does not acquire the property of combining more freely with the alkalis; it even seems to possess it in a less degree, for pot-ash, soda, and lime only weaken its penetrating odour without causing it to disappear. In this state it does not form a blue prussiate with the solutions of iron, but a green precipitate, provided the liquids are sufficiently concentrated; for this prussiate is soluble.

If this precipitate is exposed to the light it becomes blue, but it retains its green colour if it is kept in the dark: it is instantly converted to blue by pouring sulphureous acid upon it. A blue precipitate is also obtained if a little sulphureous acid is mixed with the oxygenated Prussic acid before it is used for the precipitation.

When the green sulphate is put into oxygenated muriatic acid, and a solution of prussiate of pot-ash is poured into it, the green precipitate which forms also in this case, is redissolved; it may then be precipitated blue by sulphureous acid, or by sulphate of iron, or by simply putting iron into it; so that the oxygen which changes the properties of the Prussic acid is feebly retained in it, and can easily be taken from it.

337. When

337. When a prussiate is distilled, ammonia and carbonic acid are formed, but no oil. From these products it may be inferred that Prussic acid contains azote, hidrogen, and carbon.

This composition explains the circumstances necessary to its formation: it is by calcining animal substances with the alkalis that it is produced: these substances furnish the three materials necessary to its production; the charcoals of animal substances have the same property, which proves that they retain azote notwithstanding the action of the fire: the common charcoals with which the alkalis are calcined do not yield it, or it is in so small a quantity that it can only be attributed to the small portion of animal substance which is found in most vegetables; but if muriate of ammonia is projected into this heated mixture, as was done by Scheele, then Prussic acid is formed.

It is not necessary to treat animal substances with the fixed alkalis to give rise to the Prussic acid: Scheele has proved that the liquor which he obtained from the distillation of hartshorn and bullock's blood contained it

When the Prussic acid is brought, by the action of oxygenated muriatic acid, into a state to form a green precipitate with iron, it has the property of being converted into ammonia, when it is mixed with a fixed alkali, or with lime, so that as soon as the mixture is made, there is an abundant disengagement of alkaline vapours, and, if an acid is afterwards



afterwards poured into it, the odour of the Prussic acid is not restored, which proves that it is destroyed, but carbonic acid is disengaged :

From these facts I have concluded that the Prussic acid does not contain oxygen ; that when it receives it from the oxygenated muriatic acid, the presence of an alkali is sufficient to subvert it by the formation of carbonic acid and ammonia ; and, that when a metallic prussiate, or a prussiate containing an oxide, is distilled, the oxygen which quits the metal produces the same effect as that yielded by the oxygenated muriatic acid in the experiment of which I have just spoken, and that by this the metal is more or less reduced : in fact, according to the observation of Scheele, in the distillation of prussiate of copper, the oxide was found to be restored to the metallic state. It is probable that oxi-carburated hydrogen is formed in this distillation. Scheele relates that having brought a light near to a receiver which he used in the distillation of prussiate of pot-ash with sulphuric acid, the vapour which it contained inflamed. Could the Prussic acid itself have this property ? He says that he did not succeed in obtaining it in the state of gas.

Fourcroy has opposed an observation which he made to the opinion I have offered on the composition of Prussic acid. In distilling animal substances with nitric acid he obtained Prussic acid ; whence he concluded that the nitric acid must have furnished the oxygen, which he, in consequence,

quence, considers as one of the necessary elements in its composition; but it appears to me that the formation of Prussic acid, in this case, is no more a proof that it contains oxygen, than that of ammonia, in which the existence of oxygen is not suspected, and which, in many instances, is also produced by the action of nitric acid. The properties of Prussic acid cannot themselves furnish a proof that it contains oxygen; for the substance with which it has the greatest coincidence of properties, sulphurated hydrogen, certainly does not contain oxygen (289).

It appears to me difficult to suppose the existence of oxygen in a substance which contains elements so disposed to form peculiar combinations with it, such as hydrogen and carbon, and which can sustain an elevated degree of heat without experiencing decomposition; but these considerations do not afford a rigorous proof, and we must suspend our decision on this point until an exact analysis of the Prussic acid, disengaged from every other substance, has been obtained. The following observations also add to the uncertainty which may remain on this subject; nevertheless, in the explanations which follow, I shall employ the hypothesis of a composition in which I shall not admit oxygen, but which is easily capable of the modification which oxygen would require, if its existence should be proved.

338. To conceive the formation of Prussic acid, it must be supposed capable of remaining unaffected, with the alkali with which it is combined, in the midst of a great heat, or else that it is only produced at the moment in which the azoted charcoal and alkali, which have entered into a mutual combination, are wetted, as the sulphurated hidrogen of the alkaline sulphurets is not really formed until the moment at which the sulphurets enter into communication with water. By azoted charcoal I here mean that which is obtained from animal substances, or which has the properties of it; because it is by the azote that it, in this case, produces effects different from those of common charcoal.

The latter supposition seems to me much more probable than the first. In fact, if a prussiate is exposed to a heat, less powerful even than that required for the calcination in which it is produced, it is disengaged, or decomposed; it could not therefore have supported the high degree of heat of the calcination if it had been previously formed in it.

When, after having calcined the alkali with an animal substance, it is thrown into water, ammoniacal vapours instantly exhale; and if the liquor is submitted to distillation, a considerable quantity of ammonia passes over. It cannot be supposed that this ammonia existed before the action of the water, and that it was retained by the charcoal and the alkali, to be afterwards separated

rated from them with the greatest facility; it must have been produced by the action of the water itself; there can be no doubt in this respect.

The liquid obtained by the lixiviation of the azoted charcoal, which has been calcined with the alkali, contains sulphurated hydrogen; now it is proved that the latter is only formed by the action of the water. Here, therefore, are two analogous substances which can only be produced by the assistance of the action of water.

It seems to me that the alkali begins by dissolving the charcoal, and for this requires a strong fire; sulphur is found in this charcoal, and forms a sulphuret; this being brought into contact with water, produces a sulphate and hydrogenated sulphuret.

The charcoal contains azote, which, by the concurrence of the action of the water, gives rise to ammonia and Prussic acid. The hydrogen of the water forms the first with a portion of the azote, and another portion of the latter combines with the carbon and hydrogen to produce the Prussic acid. The proportions of these two substances will vary according to indeterminate circumstances; however, a great part of the charcoal, which was held in solution, retains the oxygen of the water, and forms carbonic acid, which remains in combination with the alkali, whose action is thus divided among the Prussic acid,

acid, the carbonic acid, the sulphurated hydrogen, and the sulphuric acid.

The properties we have discovered in the Prussic acid do not admit of its being ranked with the acids. When its action is not assisted by that of the oxides, it has only a weak affinity with alkaline substances, which is very far from being able to produce that saturation, and that state of neutralization of the opponent properties which appears to me to constitute the distinctive character of acidity (37).

The name of acid can therefore only be preserved to it by an extension of the nomenclature, which is authorized by the conveniency of designating the combinations of it, which are generally very complicated.

That which appears principally to distinguish this substance is the strong action which it exercises on the oxides, and the property of forming energetic combinations with them. But the oxides offer a great difference in this respect; and it would not be easy, in the actual state of our knowledge, to determine on what conditions this inequality of action depends.

By means of the oxides, the Prussic acid acquires properties which have much more analogy with those of the acids: it usually owes this modification to the oxide of iron; but some others can produce the same effect: and Scheele cites those of gold, silver, and copper. By the action of



of the oxide, it takes a much greater state of condensation, and it exercises a resulting affinity entirely different from that which is peculiar to it. It may be conjectured, that it is the oxide itself, or rather its oxygen, which, by the solubility acquired by the oxide, and by the division of the action of the metal on this oxygen and on the Prussic acid, principally communicates to the combination the properties which approximate it to the acids.

However this may be, it has been seen that the prussiates, and particularly that of iron, are not limited to the two extreme terms of oxidation, but that, in this respect, they follow the general laws of combination; that they form and separate as soon as the opposing forces can yield to their action; and that, in the proportions of all their elements, they are subject to all the variety to which the chemical action does not offer any obstacle. The facility with which Prussic acid can form complex combinations must not be lost sight of.

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### CHAP. III.

#### *Of the Gallic Acid.*

339. THE gallic acid would not deserve particular attention for its acid properties, if its action

tion on the metallic oxides did not render it of importance to the arts, and if the knowledge of its relations with tannin, discovered by Seguin, did not serve to explain and to direct several processes; but I shall employ myself more particularly on this subject in another work: here I shall only examine the characteristic properties of the gallic acid.

The gallic acid, prepared by Scheele's process, that is to say, by extraction from the gall-nut by means of water, and by a spontaneous and slow evaporation, has only weak acid properties; it, however, forms salts which are insoluble, or but little soluble, with lime, barites, and strontian, but it is more soluble in alcohol than in water. Scheele also obtained an analogous salt, which sublimed in a distillation made very slowly and with much precaution; he obtained a considerable proportion of lamellated, white, transparent crystals: these crystals have a different taste; they have not exactly the same properties, and must not be confounded with the first acid; but they prove that the gallic acid is a substance inconstant in its composition.

In fact, if gallic acid is held in solution in water, it experiences a gradual decomposition; when it is distilled briskly, it is almost wholly decomposed, leaving much charcoal. If the solution of gold and that of silver are precipitated by this acid, the oxides which enter into the precipitates resume the metallic state.

The

The gallic acid, therefore, readily experiences changes in its composition, and the carbon, which is abundant in it, will, in its decomposition, give it the appearance of a burnt substance, in which the charcoal is become predominant.

340. Proust has applied the principles, which he adopted in the prussiates, to the combination of gallic acid with oxide of iron. According to him, the Prussic acid can only combine with the oxide of a sulphate when it is oxidized at a *maximum*. He observes, that when gallic acid, or an infusion of gall-nuts, is mixed with a solution of green sulphate, the mixture does not lose its colour, and only blackens at the surface by the contact of the air. I differ from this opinion, as well as from that of the same chemist on the combinations of the Prussic acid.

When green sulphate of iron is mixed with an infusion of gall-nuts, it is true that it does not produce a black colour, and that by leaving it exposed to the air it acquires this colour, which is propagated from the surface to the rest of the liquid. This effect is really owing to the fixation of the oxygen; but it is only necessary to dilute the uncoloured mixture with a quantity of distilled water, and it takes a black colour immediately. This change cannot be attributed to the oxygen contained in this water, for the iron must take nearly double what it contains in the state of black oxide to pass to the state of red oxide, and distilled water cannot furnish this quantity;

quantity; but this opinion may be combated by more incontrovertible proofs.

It is only necessary to add a little alkali, and the mixture immediately becomes coloured, without the contact of the air. Let a small quantity of iron filings be put into a flask full of this mixture, and it acquires colour rapidly; and when it is uncorked, some bubbles are disengaged, which doubtless are hydrogen gas.

When pulverized gall-nuts are boiled in a retort, as was done by De Laval and Priestley, hydrogen gas is disengaged, and it dissolves iron, which forms a black liquor, a true ink. In these operations the iron could not have passed to the state of red oxide, and nevertheless it formed a black combination.

A solution of iron, very little oxidized by acetic acid, immediately forms a black colour with gall-nuts.

It cannot, therefore, be maintained that the iron requires to be in the state of red oxide to be capable of combining with the gallic acid; but it cannot form with it the commencement of the precipitation to which the black colour is owing, when it is in the state of a green sulphate; because then the sulphuric acid has too much power over this oxide, and retains it too strongly. It is for the same reason that the prussiate of pot-ash cannot produce the blue prussiate, as we have seen. Let the action of the sulphuric acid be weakened by a sufficient quantity of water,  
and

and both combinations take place. With the gallic acid, pot-ash produces an effect similar to that of an acid with prussiate of pot-ash; the iron, acting on the sulphuric acid, weakens the action which it exercises on the oxide, with which it is united, so as to permit it to combine more intimately with the gallic acid. A greater oxidation is injurious to the union of the sulphuric acid with the oxide of iron, and thus favours its combination with the gallic acid.

Highly oxidized iron nevertheless produces a deeper black than that which is less so. I have given \* an explanation of this effect, which, however, I only propose as a conjecture not well founded. The gallic acid, which contains much charcoal, as is principally proved by its distillation, and which is very much disposed to experience that slight combustion, from the action of the oxygen, which, by the predominance then acquired by the charcoal, causes it to pass to a deeper or lighter colour, will undergo this combustion by the action of highly oxidized iron, as well as by the action of the oxide of silver and the oxide of gold, which it reduces, and of the oxygenated muriatic acid, which precipitates a carbonaceous matter from the infusion of gall-nuts. By this, the red oxide will pass to the state of black oxide; so that the gallic acid, by

\* Elem. de l'Art de la Teinture, Tom. I.



the state to which it is reduced, concurs with the oxide, become black, in the deep colour which is produced, while it is not changed, or is much less so, by the slightly oxidized iron of the green sulphate.

If the action of the oxygen is too strong, or too long continued, it finishes by entirely destroying the gallic acid, which leaves the oxide of iron alone, and which may then be coloured anew by gall-nuts, and especially by an alkaline prussiate, as was shown by Blagden.

The gallic acid has little solubility by itself, and forms insoluble salts with the earthy bases. It seems to me, that it is by the same property that it precipitates the oxides from their solutions, but, as its action is weak, the precipitate cannot separate in ink, and remains suspended by the action of another acid; its colour alone discovers it; nevertheless, by weakening the action of this acid by a great quantity of water, the combination precipitates; and it is by this means that Lewis and Monnet separated the combined moleculæ which give the colour to ink and to black dye.

It is evident from this why phosphoric and arsenic acid, mixed with a solution of gall-nuts, do not give a black liquor with solutions of iron; while the other acids, which do not form insoluble salts with this metal, produce it: it is because the first form a combination which is more  
insoluble

insoluble than that of the gallic acid, and which is precipitated white.

The acids dissolve the black molecularæ with more or less facility, and cause the colour to disappear; but it reappears when they are saturated by an alkali; this solution may therefore be compared to the mixture of green sulphate and gallic acid.

## SECT. IV.

*Of the Alkalis and Earths.*

## CHAP. I.

*Of Ammonia.*

341. AMONG the alkalis, ammonia is the only one which can be considered as volatile; not because pot-ash and soda are entirely deprived of volatility, there are even circumstances in which this property should be taken into consideration, but it does not act in all cases of aqueous liquidity, and in other cases it is so different from the volatility of ammonia, that these substances are, with reason, placed among the fixed alkalis, in opposition to these qualities, for the purpose of deducing the phenomena which depend on them; but they must be carefully distinguished from those which are owing to the capacity for saturation.

Ammonia

Ammonia is, besides, the only alkali whose composition is known; it is therefore proper to consider it separately under these two points of view, considering all the other alkalis as simple or undecomposed substances; for, whatever may be their composition, it has no influence on the phenomena which have hitherto been analyzed with accuracy.

While ammonia acts by a resulting affinity, it only differs from the other alkalis by its volatility; but its capacity for saturation is also much greater than that of the other alkalis (88); nevertheless, its volatility, and particularly that which it receives from heat, is a force opposed to that of combination. Its tension, at 10° of the thermometer, is 7.2, while that of water is only 0.4 inches. But this tension only expresses a small part of the force of its elasticity, because it is subdued by the action which the water exercises on it: conformably to what has been already shown, this force will augment, by an elevation of temperature, in a proportion constantly increasing (237).

It is obvious, therefore, why ammonia, which has lost its tension by combination with an acid, must regain it, in part, by the concurrence of another fixed base. Without the elasticity which it possesses, it would only divide the action of the acidity with it, in the ratio of the quantities and respective capacities for saturation; but it will be disengaged from the combination,  
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according to the volatility which is restored to it, particularly when this effect is increased by the action of heat: on this property are founded the operations by which the salts which it forms are obtained.

It is also obvious why, when the action takes place between two neutral combinations, heat will determine the separation of the combination of ammonia with the most volatile acid, notwithstanding a difference in the capacity for saturation: but I have enlarged sufficiently on these effects (156).

342. The decomposition of ammonia by the electric spark, and the subsequent combination of the hydrogen, disengaged with the oxygen, which burns with it in suitable proportions, and the azote which remains free after the combustion of the hydrogen, serves not only to determine, in a clear and easy manner, the elements which compose it, but also their respective proportions. From my experiments\*, and the results of Austin and Davy, the hydrogen forms the fifth of the weight of the ammonia: this analysis afterwards serves to explain the disengagement of the azote, when the ammonia is decomposed by oxygenated muriatic acid, or by the oxides; and the phenomena which accompany this decomposition are owing to the production of water, to the insulation of the azote, and to

\* Mém. de l'Acad. 1785.



the disengagement of part of the caloric which the oxygen contained in the prior combination.

The hydrogen is therefore combined with the azote in ammonia, in a proportion a little greater than it is with oxygen in water; but in the resulting properties of these two combinations, there is so great a difference, that it must be concluded that the affinity which unites the hydrogen and azote is much inferior to that which forms the combination of oxygen with the hydrogen.

In fact, the gaseous state retained by the ammonia when it is not subjected to the action of water, its specific lightness, which is to that of azote gas as 444 to 274, and that of the liquid ammonia, which, in its state of saturation, and notwithstanding the condensation which the water itself will experience by this combination, has only a specific gravity of 8.950, that of water being 10.000: its much greater volatility, and its much weaker disposition to congeal, prove that the condensation of its elements is much less than in water.

Its easy decomposition, either by oxygen gas, if, after being mixed with it, it is passed through a red-hot tube, or by oxygen condensed in a substance which retains it feebly, such as the oxygenated muriatic acid at every temperature, and the highly oxidized metals at the common or a more elevated temperature; and finally, its properties, which are very different from the combinations  
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of those whose elements have experienced a great saturation, prove it incontestibly.

Nevertheless, when ammonia exercises its alkaline property on an acid, in which the oxygen is a little more powerfully subdued than in oxygenated muriatic acid, its composition is maintained by the resulting force of this combination, until it is sufficiently weakened by heat: thus nitrate of ammonia preserves its constitution to an elevated degree of heat; then it is decomposed, and gives birth to new combinations.

Ammonia combined with sulphuric acid, or with the other acids which can yield oxygen, also experiences a decomposition at a high temperature; but it has been but little examined.

The power of action exercised by the hydrogen on many substances, which is, in general, much greater than that of azote, and particularly the force with which it acts on oxygen, render it probable that it is the principle of the alkaline energy possessed by the ammonia, or of its strong tendency to combination with the acids; but no general conclusion can be formed on the alkalinity, which may be owing to different causes.

343. The correspondence of composition of nitric acid and nitrous gas with ammonia, enable us to conceive how they can serve mutually for their production, according to the circumstances in which they are found, and which I shall detail. But these opposite results show more and more how false an idea of chemical causes is formed

formed by considering the affinity as determined by the nature of the substances alone, and as the invariable principle of the combinations which are produced.

Priestley, Higgins, Guyton, Austin, Kirwan, and several other chemists have shown that ammonia was formed in different circumstances, by means of nitric acid or nitrous gas. Austin observed that this formation could take place immediately with azote gas, when a substance, such as that of iron-filings, solicited the decomposition of water; but this production takes place more especially with nitrous gas, while this is converted into gaseous oxide of azote; it is easier when sulphurated hydrogen gas is mixed with nitrous gas.

On the other hand, Milner observed\* that when ammoniacal gas was passed through oxide of manganese contained in a red hot tube, nitrous gas was produced: Vauquelin, Seguin and Sylvestre obtained nitrate of ammonia by this means, and Fourcroy has shown that the same production took place without foreign heat when a mercurial precipitate was treated with ammonia†. Besides, while Milner formed nitric acid or nitrous gas, by passing ammonia through highly oxidized metals, Haussman, on the contrary, produced ammonia by passing nitrous gas through iron-filings but

\* Philos. Trans. 1789.

† Ann. de Chim. Tom. VI.

little oxidized : in the one case, the metal could yield the oxygen for the formation of nitric acid ; in the other, it must have decomposed the water which accompanied the nitrous gas, and so have occasioned the production of a little ammonia.

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## CHAP. II.

### *Of the comparative Properties of Alkalis and Earths.*

344. WHEN the chemical properties of bodies began to be examined, the name of alkali was given to those which were capable of forming combinations with the acids, and they were distinguished into fixed and volatile : those substances only were considered as fixed alkalis which had a great solubility in water, that is to say, pot-ash and soda, although other substances had properties which were similar and even superior with respect to the faculty of forming saline combinations : but those were blended under the name of earths, which retained an appearance of siccidity, or of insolubility, distinguishing however those which could be dissolved by the acids, and which were called alkaline earths, absorbents, or earthy bases, from those which have not this property.

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In the substances which have been arranged among the earths, some are found to which this name has only been given on account of some of their combinations which are insoluble, while they have themselves a solubility which greatly resembles that of pot-ash and soda.

The distinctions established on these vague ideas, and in which the real alkalis are blended with the earths, and combinations with simple substances, are not reconcileable with the chemical properties, whose relations are employed in the classification of bodies.

In following these relations, all those substances must be ranked among the alkalis which can by themselves produce a complete saturation of the acids, rendering their acidity latent by an opposing property which constitutes alkalinity.

These substances are ammonia, magnesia, lime, pot-ash, soda, strontian, and barites; their alkalinity, which follows the order in which I have named them, is measured by their capacity for saturation (81).

The first distinction between these alkalis is founded on the volatility and fixity: ammonia alone can be considered as volatile.

Another distinction may be established between the fixed alkalis, on their solubility and their force of cohesion: pot-ash and soda are the fixed alkalis which are, at the same time, the most soluble in water, and, by the properties of their combinations, announce the least force of cohesion.



After pot-ash and soda comes barites, which requires only 20 parts of water to be held in solution at a temperature of  $10^{\circ}$  Reaum. : strontian requires 200, and lime 500. Magnesia is the most insoluble ; but as the insolubility of a substance is compounded of the weak action of water, and of the resistance of the force of cohesion, it cannot be determined, by this consideration alone, which of these alkalis has really the greatest force of cohesion, or whose moleculæ exercise the greatest reciprocal action : to judge by the qualities of their compounds, barites seems to be superior in this to the others ; but it is difficult to be guided by the properties which the combinations offer in this respect, because they arise both from the dispositions of the alkaline base, and from the quantity which is necessary to saturate the acid ; besides the form taken by the integrant moleculæ, or some other slight condition of the combination, may occasion some variation in the force of cohesion, so that by being confined to a vague determination on this subject, we are compelled to judge of the preponderance of each of these bases, in the particular instances, by the comparative properties of their combinations.

All these alkalis have the property of producing insoluble, or slightly soluble salts with those acids which have themselves a disposition to solidity, such as the phosphoric, fluoric, oxalic, citric, and saccho-lactic, and those which produce a soluble combination

combination with the other acids precipitate by forming an insoluble combination as soon as the action of the acid is weakened by the concurrence of another alkali, while pot-ash and soda, which do not yield any insoluble salt, do not form a precipitate in the same circumstance; hence it arises that barites, for example, being more soluble, produces a precipitate in the solutions of strontian; which has been the occasion of an inferior affinity being attributed to the latter, although it has a greater capacity for saturation (199).

The disposition to form insoluble salts is sometimes disguised in these alkalis, by the neutral combination becoming soluble in an excess of acid, or because, to attain the neutral state, they require a quantity of some of the acids little disposed to solidity, which overcomes their natural disposition, but it is manifested as soon as the action of these acids is weakened.

This difference between the alkalis authorizes the retaining the distinction of fixed alkalis and earthy bases, provided it is confined to indicating the dispositions to solidity which they possess in themselves, or communicate to their combinations.

345. These alkaline bases are not always expelled from the combinations which they produce with the acids; some of them form triple salts, so that an acid produces a combination which is uniform, and crystallizes regularly, with two bases: this is a property which belongs particularly to ammonia and magnesia, and which in

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my opinion should be attributed to the force of their affinity; but whatsoever may be the cause of this effect, it should engage our attention, and the more so as it can easily lead to error, when it is required to determine the proportions of substances which form a compound.

Bergman had remarked the property of magnesia, as well as some of the oxides, of giving triple salts with ammonia, but we are indebted to Fourcroy for some important observations on this subject.

Fourcroy has shown \* that it required a certain quantity of ammonia for a salt with base of magnesia to begin to abandon a portion of this base, and that by augmenting the quantity of the ammonia, but far beyond what will enter into the salt which crystallizes, all the magnesia which could separate, might be precipitated, but that it would not exceed a certain proportion. The salt obtained by crystallization contains a proportion of acid, corresponding with that which the same quantity of magnesia and ammonia would have saturated, although it differs in the proportions of these two bases, according to the circumstances of the operation: in fact, if the state of saturation is unchanged, if the triple salt is in the neutral state, as it is supposed the separate salts of magnesia and ammonia are, it cannot be conjectured that these two bases exercise a mutual action

\* Ann. de Chim. Tom. IV.

which

which leads to any change in their alkalinity. Fourcroy supposes that the precipitate which is formed is pure magnesia; it probably retains some of the acid, and perhaps of the ammonia, as unquestionably is the case with the oxides.

Fourcroy also observed\* that in a triple salt produced by an oxide, the proportion of acid was not the same as in the salt formed by the oxide and the acid, and in that with the ammonia and the same acid, but that the triple combination retained a smaller quantity of acid; he also found that sulphuric acid was set free when he formed the ammoniaco-mercurial sulphate by precipitating a very neutral sulphate of mercury by the mixture of its solution with that of sulphate of ammonia also in a neutral state: this effect does not agree with those I shall exhibit on the reciprocal action of metallic salts, and salts with an alkaline base.

The triple salts are not limited to determinate proportions, although there is a constant relation between the quantities of the bases and those of the acids which produce their saturation, but many varieties may be obtained in which the proportions are different, and the crystallization also takes different forms, but this has very little dependence on the changes of the proportions.

346. All the alkalis have, directly or indirectly, the property of forming combinations with sulphur; but the instability of these combinations,

\* Mém. de l'Acad. 1790.

the characteristic properties of sulphur which depend on its affinity for oxygen, and which are not neutralized by the alkalis, require that they should be distinguished from the saline combinations, although when separated from the oxygen, they have so much correspondence with them, that the results of observation on the reciprocal action of acids and alkalis, may be applied to the mutual action of their elements.

If, therefore, sulphur cannot combine directly with all the alkalis, the cause of this must be sought in its force of cohesion, and in the resistance it may experience in the dispositions of the alkali.

The obstacle arising from its force of cohesion no longer exists in sulphurated hydrogen, which seems to owe the acid qualities it possesses only to the sulphur itself (293), sulphurated hydrogen has not only the property of combining with the alkaline bases\*, but all the combinations it forms with them have that of being soluble in water; they are analogous to the combinations of the acids and alkalis; some of them are also capable of taking the form of crystals.

To comprehend the varied combinations which sulphur and sulphurated hydrogen can offer with different bases, and the phenomena which depend on them, the attention must be directed to the following properties.

1st. Sulphur cannot remain alone in a liquid combination with the alkalis, for if the sulphu-

\* Ann. de Chim. Tom. XXV.



rated hydrogen, which serves to retain it in aqueous solutions, is destroyed by oxygenated muriatic acid, by nitric acid, or by sulphureous acid, the sulphur immediately precipitates. The sulphurets, therefore, can only exist in a state of desiccation, or, at least, if they can contain water, without it being decomposed, the quantity must be very small. The separation of the sulphur, when the sulphurated hydrogen is destroyed, must not be attributed to a want of affinity for the alkali, but partly to the force of cohesion of the sulphur, and partly to the great affinity of the alkali for water.

2d. Sulphurated hydrogen, which I consider in this place independently of the differences which may be found in its composition (291), has such an action on sulphur that it can dissolve it, and form the liquid combination, which I have called hydrogenated sulphur: but the sulphurated hydrogen which has a strong tendency to elasticity, easily separates by heat, or by the dissolving action of the air, and abandons the sulphur which it had taken in solution and rendered liquid. On the other hand, sulphurated hydrogen forms combinations with the alkalis which are more durable than those of sulphur, or rather which are not destroyed by water: in this instance we cannot overlook the property of hydrogen of weakening the force of cohesion, and causing its effects to disappear: this influence of the hydrogen is found in the hydrogenated sulphurets, which may be considered as the combination

nation of an alkali with hydrogenated sulphur, a combination which is variable because it is not very energetic, and which may be obtained by different means ; 1st, by the solution of hydrogenated sulphur ; 2d, by the solution of sulphur by an hidro-sulphuret ; 3d, by the decomposition of water produced by a sulphuret.

I have observed that when an hidro-sulphuret is left exposed to the air, sulphureous acid is formed (290) : in this circumstance the action of the alkali prevents the sulphureous acid and sulphurated hydrogen from being destroyed, in the same manner as the hydrogen of ammonia is preserved with the oxygen in nitrate of ammonia ; but as soon as the resulting action of the alkali is weakened by the addition of an acid, sulphureous acid and sulphurated hydrogen are destroyed, water is formed, and the sulphur of both precipitates ; during this precipitation, the odour of sulphureous acid is not perceived, because it is decomposed ; but that which is afterwards disengaged is developed.

347. These observations seem to me to account for the composition of a singular salt which is formed in the operations of the manufactory of Citizens Payen, and which has given rise to a discussion between Chaussier and Vauquelin\*. This discussion is important from the intelligence of the philosophers between whom it took place, and because it concerns a peculiar species of combi-

\* Ann. de Chim. Tom. XXXII.

nation, and can throw a light on many phenomena analogous to its formation: Chaussier has called this salt sulphurated hidro-sulphuret of soda, and this denomination sufficiently indicates the opinion which he has formed of it: Vauquelin has called it sulphurated sulphite: he proves effectually, by convincing experiments, that sulphureous acid exists in it; but I differ from his opinion of the other element, which appears to me to be sulphurated hydrogen, and not sulphur.

This salt is formed by mixing water charged with sulphurated hydrogen with a solution of sulphite of soda; my associate supposes that all the sulphurated hydrogen is decomposed; but sulphureous acid and sulphurated hydrogen have only the property of mutual decomposition when they are free; the action of an alkaline base prevents this effect from taking place, or rather, limits it, as is unquestionably proved by the formation of sulphureous acid in a hidro-sulphuret which is left exposed to the air, as I have just mentioned, and which also takes place in an hydrogenated sulphuret which is exposed to the air. The hidro-sulphuret has lost only a part of its properties, and, nevertheless, the sulphureous acid exists in it with the sulphurated hydrogen; so that one does not decompose the other, when their action is diminished by that which they exercise on an alkaline base.

This action of the resulting affinity of the alkali only extends, however, to a certain degree; if an  
excess

excess of sulphurated hydrogen is added it can produce a decomposition, as is seen in the experiments of Vauquelin, and an excess of hidro-sulphuret remains, which causes the liquid to resemble a hidro-sulphuret which has been left exposed to the air, and in which sulphureous acid has formed; whence it results that to produce the hidro-sulphurated sulphite, without the liquid being rendered turbid by a precipitation of sulphur, there must not be more than a suitable proportion of sulphurated hydrogen.

It may, however, happen that even when the liquid does not become turbid, some decomposition really takes place: the neutral state in which the salt remains seems to indicate it, for there should be an excess of acidity from the combination of the sulphurated hydrogen: in this view of it, therefore, a portion of sulphureous acid, corresponding to that of the sulphurated hydrogen, and of sulphur, which would have served to neutralize a corresponding portion of the alkali, must have been destroyed; but it seems to me much more probable that the reciprocal action of the sulphureous acid, and sulphurated hydrogen, though it is not sufficient to operate their decomposition, weakens, nevertheless, that which each of them exercises on the alkali; so that the neutral state is unaltered. It is thus that the mutual action of the oxygen, and muriatic acid hinders their combination from producing any change in the neutral state of the muriate compared with the super-oxygenated muriate of

of pot-ash (181); what confirms me in this opinion is, that the hidro-sulphurated sulphite does not acquire any colour, while the hidro-sulphuret, exposed to the air, soon contracts a yellow tinge, which is owing to the sulphur becoming predominant in the composition of the hidro-sulphuret.

The same phenomena, therefore, are observed in the hidro-sulphurated sulphite in question, as in the hydrogenated sulphuret, or in the hidro-sulphuret, in which sulphureous acid is formed: if an acid is only added in small portions, the sulphureous acid, set at liberty, acts on the sulphurated hydrogen, and a mutual decomposition takes place, so that no sulphureous vapour exhales; it is only when this effect has ceased, that the disengagement of sulphureous vapour is produced by the addition of a greater quantity of acid; the only difference is, that when the hidro-sulphuret is decomposed, hidro-sulphurated gas exhales; which only takes place with concentrated sulphuric acid, when the experiment is made with the hidro-sulphurated sulphite, because, compared with the hidro-sulphuret, it contains an excess of sulphureous acid.

When the hidro-sulphurated sulphite is urged by fire, the resulting affinity which maintained its composition is destroyed; the sulphurated hydrogen and sulphureous acid are decomposed; whence results the formation of a more abundant sulphuret than when a sulphite is submitted to the action of the fire; a part of the sulphite is also changed



changed into a sulphate, and I am convinced that sulphurated hydrogen gas is also disengaged.

Vauquelin produced this salt by boiling a sulphite with sulphur, and he used this experiment to support his opinion, but he has himself observed that the liquid then contained a sulphate, so that sulphuric acid is formed, as when a sulphuret is placed in contact with water, and for the same reason sulphurated hydrogen would be produced.

He considers the sulphurated hydrogen gas, which is disengaged by the action of concentrated sulphuric acid, as a result of this action; but all the circumstances are then unfavourable to this production, and particularly the disengagement of sulphureous acid which would destroy it entirely, if the rapidity of the disengagement permitted it.

348. If the force of cohesion belonging to the sulphur is an obstacle to its combination with the alkalis, which have great solubility, this effect will be much greater when the same insolubility is found in the alkali; it therefore is not surprising that magnesia, notwithstanding its powerful action on the acids, can only form a combination with sulphur with difficulty, and by keeping it a long time at the heat of ebullition in a vessel filled with water\*. But sulphurated hydrogen can dissolve magnesia, and form a hidro-sulphuret with it. It is probable that this hidro-sulphuret is ca-

\* Bergman, *De Magnesid.*

pable of dissolving sulphur, as it is seen that this takes place with ammonia, which it resembles in the energy of its affinity.

Ammonia itself cannot dissolve sulphur, because its volatility does not admit of a degree of heat being employed which would weaken the force of cohesion of this substance sufficiently; but it shows the power of its affinity when it is combined with sulphurated hydrogen, and forms a hidro-sulphuret; for this hidro-sulphuret can dissolve so large a quantity of sulphur, that the solution acquires a yellow colour, and an oily appearance\*.

When the hidro-sulphuret of ammonia has ammonia in excess, it is fuming, and analogous to the fuming liquor of Boyle, except that this holds sulphur in solution. There is no marked difference between the hidro-sulphuret, and the hydrogenated sulphuret of ammonia; but the hidro-sulphuret which has much sulphur in solution, and which forms a yellow liquid, may be distinguished by the latter denomination.

A difference is observed between the action exercised by barites and strontian on sulphur, which seems capable of being also explained by the difference of their solubility: if, after having exposed the sulphuret of strontian to a heat rather strong to oblige the sulphur to abandon it in part, the combination is boiled in a sufficient quantity of water,

\* Ann. de Chim. Tom. XXV.

a part of the strontian crystallizes and separates from that which remains in the state of hydrogenated sulphuret\*, so that the force of crystallization being in opposition to the affinity of the sulphur and the sulphurated hydrogen, produces a separation of the two combinations; but this force being much smaller in the barites, the separation cannot take place. This property of strontian gives the means of separating it immediately from a sulphuret formed with sulphate of strontian; but to produce this effect with the hydrogenated sulphuret of barites, a substance must be added to it which can decompose the hidro-sulphuret, and form an insoluble combination with the sulphur.

The properties which sulphur communicates to the numerous combinations which it can form, and those which they acquire themselves, take therefore their origin, 1st, from its affinity for oxygen, which is predominant; the acid resulting from their mutual action varies according to the condensation which the oxygen receives; 2d, from its affinity for hydrogen; 3d, from that which it has for the alkaline bases. The elements united by these affinities exercise a mutual action which produces variable combinations, or rather the combinations formed are liable to changes according as they meet either of the elements between which this action can be exercised.

\* Journ. de l'Ecole Polytech. XI<sup>e</sup>. Cahier.

349. The other earths are distinguished from those whose properties require them to be placed among the alkalis, by the difference of their action on the acids; even those which can dissolve in the acids have not the property of forming neutral combinations which can give a method of comparing their capacity for saturation; the resistance of their force of cohesion, even when they are in their greatest state of division, is sufficient to prevent the weak acids from operating their solution: besides this they have more or less the property of combining with the alkalis, so that they seem to hold a medium between the acids and the alkalis, and thus to approximate to the properties of oxides; but their common characters are too little marked for them to be treated by their general properties; each species must therefore be considered in particular.

Alumine has nearly an equal disposition to combine with acids and alkalis; but its force of cohesion must not occasion too great an obstacle to these two species of combination; thus carbonic acid cannot dissolve it immediately; it even abandons it when it is precipitated from an acid solution by a carbonate, and it passes to the solid state: at least it seems only to retain it, according to the observations made by Theodore Saussure, in a very interesting memoir on alumine, in proportion to the alkali which it retains in its precipitation; but liquid carbonic acid can dissolve a small quantity of it.

A proof that this difficulty of solution only depends in reality on the obstacle opposed by its force of cohesion is, that acetic acid, which scarcely dissolves alumine, can combine with it if the sulphate of alumine is mixed with acetite of lead: the oxide of lead forming an insoluble salt with sulphuric acid, the alumine remains in combination with the acetic acid which makes an exchange of base, but sulphurated hydrogen cannot dissolve alumine, and consequently may serve to separate it from alkaline earths.

Of all the combinations which alumine produces that which it forms with sulphuric acid deserves the most attention, both for the properties which distinguish it, and for the importance of having an exact knowledge of it, either for chemical analysis, or, principally, for its employment in the arts.

Bergman had observed\* that alum usually contained pot-ash, and that it was useful to its crystallization; but his opinion was not limited to its effect, he believed that it served to absorb an excess of acid, and that alumine could supply its place; nevertheless, he announces elsewhere that pot-ash and ammonia, in the state of a neutral salt, produce the same effect.

Chaptal, who threw so much light on the arts, and showed how advantageous chemistry could be to them, before the protection which government

\* De confect. alum. de platina.



affords to them was entrusted to him, experienced in the operations of his manufactory\*, “that without the assistance of alkalis only a magma, or granulated precipitate, was obtained, which showed no appearance of crystallization;” and that the advice given by Bergman to saturate the excess of acid of an aluminous liquor by alumine, which he supposed augmented the quantity of crystallizable salt, was not practicable: “If the acid lixivium is boiled with clay baked or unbaked, the dissolution is only made very slowly, and by a strong ebullition; when the lixivium appears to be saturated, if it is filtered, it allows a great part of the clay which it had dissolved to precipitate by cooling; if, in this state, the solution is concentrated, the clay is disengaged, and forms a precipitate which opposes all crystallization.”

In the course of the operations which he was aiming to bring to perfection, he found that sulphate of pot-ash might be advantageously substituted for pot-ash, and Decroizille made the same observation: he also discovered that sulphate of ammonia produced a similar effect.

Vauquelin, on his part, has observed†, that, with sulphuric acid, alumine only formed a granulated and lamellated substance, which could not be made to crystallize; that pot-ash or ammonia

\* Mém. de l'Acad. 1788. Ann. de Chim. Tom. XXII.

† Ann. de Chim. Tom. XXII.

were necessary to crystallization ; that their sulphates answered the same purpose ; that in the Roman alum it is pot-ash alone which produces the crystallization ; and that the greater part of the others contain pot-ash and ammonia at the same time : he estimates the quantity of either of these alkaline sulphates found in alum at seven per cent. ; but it is probable that this quantity varies both in pot-ash and in ammonia ; this has not yet been determined. From his observations he has drawn this important consequence for chemical analysis, that in all cases when crystals of alum are immediately obtained from an earthy substance, by means of sulphuric acid, this substance contains pot-ash, and he has thus proved its existence in many stones in which it was not suspected. This proof shows that the generality of clays and marles hold a little pot-ash ; at least I have always obtained crystals of alum from the several species which I have assayed.

The sulphate of alumine is therefore necessarily a compound salt ; but besides pot-ash and ammonia, it can also receive different proportions of acid. I have dissolved crystals of alum, transparent and permanent in the air, of different manufactures, and by causing it to crystallize, have obtained a residue which contained a more or less considerable excess of acid : I have sometimes obtained acidulous sulphate of pot-ash from this residue, which crystallized separately, and especially by efflorescence.

This

This salt, on the contrary, can also contain an excess of base, and it then acquires the property of crystallizing in cubes, as was observed by Vauquelin, and as had been remarked before by Siefertz.

Finally, alum may contain a certain quantity of sulphate of iron. It is therefore evident how many variations this salt may receive in its composition without its transparence, its crystallization, or its other apparent properties indicating them.

It is known that the Roman alum and that from the Levant, are preferred to the others for brilliant dyes: I presume that this advantage over the alums fabricated by the immediate combination of the acid and the alumine, depends principally on the excess of acid which I have found in the different species of manufactured alum, although this excess is not perceptible either by the form of the crystallization, or by the hygrometric properties.

The decomposition of alum also gives variable results: if its base is separated by a carbonate, the precipitate retains a considerable proportion of acid, and even of the alkaline base; for by dissolving it in nitric or muriatic acid, alum is obtained by crystallization; if, on the contrary, alum is precipitated by an alkali, and, particularly, if after the precipitation it is kept in digestion in an alkali, a much smaller quantity of the sulphuric acid is retained; nevertheless if the precipitate is dissolved in nitric acid, the solution still forms a sulphate with solution of barites (63).

Vauquelin

Vauquelin decomposed sulphate of alumine by alumine, and found that the insoluble salt which formed, and which had been observed by Baumé, in addition to the acid, retained some alkali in its composition.

Soda can also enter into the composition of sulphate of alumine, and give it the property of crystallizing, as was observed by Berard, according to the relation of Chaptal; but the crystals which I have examined are more soluble than those of alum, and effloresce in the air.

Nitric acid has likewise the property of crystallizing with alumine: it is probable that this is also by means of an alkaline base.

350. Alumine dissolves in pot-ash and in soda, provided its force of cohesion does not offer too considerable a resistance: this solution supports evaporation without the alumine being disengaged. This property of entering into combination with the alkalis, notwithstanding its disposition to take the solid state, serves to explain the effect by which the alkalis, as we have just seen, strengthen its combination with the acids; they exercise their affinity on the alumine and on the acid: this reciprocal action of the alkalis and of alumine also explains why the precipitates of alum carry with them the alkali, which has been employed as a precipitant, and perhaps why an alkali is found in a great number of earthy compounds, in which a certain proportion of alumine is found.

Lime,

Lime, which a slight solubility permits to act only in a small quantity, showed a disposition to unite with alumine, in the experiments for which we are indebted to Scheele\*. Lime-water having been poured upon alumine, precipitated alum, which, from his description, was in a gelatinous state; all the lime was combined with it: the solution of sulphate of lime having been put to the same alumine, did not form a combination; but on adding lime-water, not only the lime, but the sulphate of lime, was entirely precipitated, and formed a combination which may be considered as analogous to that of alum, or rather of insoluble sulphate of alumine, since it was formed of alumine, sulphuric acid, and lime.

The affinity of lime for alumine is also shown when a combination which holds alumine and lime in solution is precipitated by ammonia: the latter, which would not have been precipitated by ammonia, is partly separated with the alumine.

The weak condensation which ammonia is capable of with water, compared to that of pot-ash and soda, explains its inaction on alumine; nevertheless, it dissolves a little of it when it is extremely divided†, and its action is particularly shown in the triple salts which it forms with it, as we have seen in the sulphate of alumine.

The insolubility of magnesia prevents it from exercising its alkaline action in ordinary circum-

\* Mém. de Chim.

† Syst. de Conn. Chim. Tom. II.



stances, but we have a proof of the alkaline action which it exercises on it, when its cohesion ceases to be an obstacle; thus when a solution of magnesia and alumine is precipitated by ammonia, the magnesia which would have remained in solution, and would have formed a triple soluble combination with the ammonia, until the proportion of the latter had become so great as to separate a part of it, is entirely precipitated with the alumine, and then pot-ash or soda, which could have dissolved the precipitated alumine, if it was uncombined, cannot separate it from the magnesia, or only dissolve a part which is not retained with sufficient power by the magnesia, according to the observation of Chenevix\*: alumine shows some action on silex for if it is in sufficient quantity, it favours its solution in the acids.

Strontian and barites, whose alkaline action is much weaker, cannot overcome the obstacles which oppose their combination with alumine; and the precipitates which are obtained from the mixture of the solutions of alumine and barites, are only owing to the sulphuric acid which the alumine had retained in its precipitation, as has been shown by d'Arracq and Chenevix; but strontian cannot indicate these small quantities of sulphuric acid, because the sulphate which it forms has more solubility than that of barites.

This reciprocal action of alumine and the alkalis is useful in the decomposition of salts which con-

\* Ann. de Chim. Tom. XXVIII. Philos. Trans. 1802.

tain a fixed alkali and a volatile acid, such as the nitrate of pot-ash and the muriate of soda. The alkaline base directs part of its action on the alumine, and thus, that which it exercises on the acid is diminished, while the tension of the latter is increased by the heat, and finishes by producing its separation, conformably to the theory which I have laid down on distillation (245).<sup>1</sup>

351. The action of alumine on water is considerable; but it varies according to the state in which it is found, as is proved by the important experiments of Theodore Saussure. This skilful philosopher has noticed that the alumine acquired an appearance and properties, differing according to the circumstances of its precipitation from sulphate of alumine\*; if the quantity of water does not exceed what is necessary to dissolve the sulphate of alumine, which is precipitated by ammonia or by carbonate of ammonia, the product is a white, light, friable, very spongy earth, which adheres to the tongue; he calls it *spongy alumine*. But if the aluminous salt is dissolved in a very great quantity of water, the mass obtained, after drying the precipitate, at the same temperature, is transparent, yellow, and brittle, which has not an earthy appearance, which does not at all adhere to the tongue, which, with the same weight, occupies a volume ten or twelve times less than the spongy alumine. It resembles gum Arabic or a dried jelly :

\* Journ. de Phys. Tom. LII.

he calls it *gelatinous alumine*. It is to be wished that he had examined whether this difference does not depend on the proportions of acid which the alumine might retain in the two circumstances.

There must, without doubt, be intermediate states of combination of alumine with water; but the precipitates obtained in the analysis will most frequently resemble the gelatinous alumine.

Spongy alumine and gelatinous alumine contain the same quantity of water, when they are dried at the temperature of the atmosphere; but the first retains it much less strongly, and abandons it at a much lower heat: at a red-heat, but inferior to that which causes silver to enter into fusion, 100 parts by weight of spongy alumine lose 58 parts: 100 parts of gelatinous alumine lose only 48 and a quarter, at 130° of Wedgwood's thermometer, and but 43 parts at the degree of incandescence.

Saussure considers the spongy alumine which has lost the 58 parts of water, as absolutely deprived of this substance, which does not appear to me to be proved; it is even probable that it retains some portion of it in the same state as that which is united to the gelatinous alumine; that this water resists the action of heat, and that it could still be manifested, in both of them, by some method which would produce its decomposition, that is to say, by the action of some inflammable substance.

He is of opinion that Wedgwood's pyrometric cylinders lose all their water by the first degrees of heat: he submitted one to the action of the fire which sustained no sensible loss from  $29^{\circ}$  to  $170^{\circ}$ . But he found, as he has himself observed, a great difference in these cylinders: Wedgwood was able to carry those which he proved to  $240^{\circ}$  and he observed that one cylinder lost nearly two grains in the latter parts of the scale: now so considerable an error in a fact cannot be suspected in a philosopher of such experience.

Saussure's experiments show how much uncertainty may remain on the determination of the alumine in chemical analysis: a gelatinous alumine, carried to incandescence, a degree to which the alumine obtained in an analysis is rarely carried, still contains 0.15 of water. In consequence of his experiments, he only makes the alumine in sulphate of alumine to amount to 0.09, and in this estimate he neglects the acid which must be retained in the precipitate.

Although, from these experiments, alumine shows that it has a great affinity for water; that several properties are dependent on it, and particularly the flexibility and tenacity which it has when it does not contain any acid, and which render it so useful in the arts, the action which water exercises on it is nevertheless insufficient to effect its solution; which shows how important the consideration of the force of cohesion is to discover the affinities which, latent in some circumstances,

stances, become active in others, and produce effects which are afterwards attributed to foreign causes.

352. Silix has more disposition to combine with the alkalis than with the acids: if, when it is recently precipitated, it is boiled with pot-ash, a considerable quantity of it is dissolved, while, in the same circumstances, it is not dissolved by sulphuric acid\*.

Although its force of cohesion does not seem more considerable than that of alumine, since the sapphire and corundum have more hardness than stones in which silix predominates; it nevertheless, in general enjoys much more of this property, because it has but little affinity for water, while alumine has a great one: if silix is found in several waters, it is only by means of the action which the salts exercise upon it; thus Black has shown that the waters of Geyser contain a little pot-ash, by means of which they hold silix in solution.

Its force of cohesion is an obstacle to its combinations which is so much the more efficacious when this force is met with at the same time in the alkalis: hence it arises that silix only dissolves in pot-ash and soda, which can form a liquid in which they are much condensed: this is probably the cause which prevents its solution by lime, for the properties of mortar prove that these two sub-

\* Bergman, *de terra siliceâ op.* Tom. II.



stances act with energy on each other: the action of barites, of strontian, and of magnesia on silex is not yet known.

When an acid is mixed with silicated pot-ash, the effects differ according to the quantity of water: if the silicated pot-ash is only dissolved in sixteen parts of water, sulphuric acid does not produce any precipitate in it: it requires at least twenty-four parts of water for a precipitation to take place: the saline combination acts sufficiently on the silex to retain it in solution in the first case; but the difference of solubility at length produces a separation in which the sulphate remains with the water; the silex, however, retains a portion of pot-ash which renders it fusible before the blow-pipe, as was observed by Bergman. The water only destroys the combination of the pot-ash and the acid with the silex by the superior affinity it possesses for the two first elements; but its effect is subordinate to its quantity.

All the acids can dissolve silex, but only when its force of cohesion is very much weakened by the action of a solvent, such as pot-ash or soda; so that after having produced a precipitate, they redissolve it, if it has not sufficient time to agglutinate: they retain the silex so much the more strongly as the action they exercise is more powerful: thus, in this respect, the muriatic acid is superior to all the others, except the fluoric acid; but although there is no excess of acid, since both the acid and the alkali act on the silex, their combination

bination has the property of retaining it in solution, until, by desiccation, its force of cohesion is sufficiently augmented to resist their action ; hence arise the gelatinous residues obtained by evaporating the solutions formed in the analysis of several minerals, and from which the silex is not separated until after a strong desiccation.

The fluoric acid, whose power is very great (87, also acts more on silex by it than the other acids : it dissolves it notwithstanding the cohesion which it has in glass ; it carries off a part of it in the state of gas ; nevertheless, when the gas which is charged with it combines with water, the action of the latter causes it to abandon a part of the silex, which, in precipitating, very probably retains a little fluoric acid, as is indicated by the following experiment, and particularly by the analogy with other combinations which the action of water divides into one which is more soluble, and one which is less so, by the difference of proportions which it establishes.

When fluoric acid is saturated with an alkali, holding silex in solution, the precipitate which is formed, not only contains a little fluoric acid, according to the observation of Bergman, but it forms a triple combination which is a little soluble in water, and much more fusible by heat than that which is only precipitated by water.

353. Glucine, for whose discovery we are indebted to Vauquelin, has a resemblance in character to alumine ; it, however, seems to have much  
more

more disposition to combine with the acids; the saccharine taste acquired by its combinations seems to announce a great saturation, so that it may really be alkaline. The property which it has of forming a triple combination with the carbonate of ammonia was employed by the learned chemists who discovered it to separate it from alumine; but this combination is weak, as the sole action of ebullition is sufficient to precipitate the earth and separate the carbonate of ammonia from it.

Zircon, discovered by the celebrated Klaproth, seems to have less action on the acids, in which it does not dissolve unless it is in a state of great division: it easily abandons them by the action of heat: it forms an insoluble salt with sulphuric acid: it is not attacked by the alkalis; their action, however, combined with that of carbonic acid, can effect its solution when it is very much divided: it may be said to be already in a state of saturation.

The gadolinite has been so little examined hitherto, that the properties which may serve to distinguish it are but imperfectly known.

Thus among the earths, some possess all the properties of alkalis; they can only be distinguished by the variable effects of the force of cohesion. It is not even their own insolubility which has served to establish their distinction from the alkalis, but that of some of their combinations.

The

The insolubility, which may be united with a very great alkaline power, has led to the separation of magnesia from the alkalis, although it yields only to ammonia in its capacity for saturation.

We have noticed earths which, by their properties, are removed from those which possess the alkaline properties in their integrity; these must be distinguished as particular substances: they have not therefore any general character, but each has its peculiar habitudes with other substances; nevertheless, their properties are principally derived from their relations with the acids, with the alkalis, and with water, and from their force of cohesion.

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### CHAP. III.

#### *Of the mutual Action of the Alkalis and Earths in Liquefaction.*

354. I HAVE examined the properties of alkaline substances, without having neglected their secondary affinities; I have considered the property of neutralizing acids as their predominant character; I have compared their capacity for saturation; I have endeavoured to determine what influence their degree of solubility might have in the different circumstances, but independently of a strong heat. While saturation veils the alkalinity, the insolubility

insolubility which marks the character of the earths, uniting with parallel qualities in the acids, is the principal cause which determines the properties of the combinations which they form with the acids, and which, in the neutral state, directs the choice which each base can make between different acids to produce the same degree of saturation (71). This insolubility, which serves to distinguish the earths when it is absolute in a substance, or when it is found in such of its combinations as have principally engaged attention, is not always accompanied by the complete properties of the alkalis, but we have noticed earthy substances which have only imperfect alkaline qualities, or which have even tendencies to combination analogous to those of the acids, and which, either with the acids or the alkalis, offer only properties which are peculiar to them: by this we have distinguished them from the alkalis.

In this chapter I shall examine the mutual action which these different substances can exercise when they receive the liquid state by heat alone, and, consequently, the obstacle of cohesion is removed.

In the mutual action which the alkaline and earthy substances can exercise by the assistance of heat, it is much more difficult to separate the effects arising from the tendency they have to combine together, from those which are produced by the reciprocal action of the *moleculæ*, than



in the phenomena which we have hitherto examined: 1st, because they always take place between substances whose force of cohesion becomes at once very great, as soon as the cause of its disappearance is diminished: 2d, because the intensity of this cause, which is the expansion by heat, varies in a very extended scale, of which it can pass rapidly through the different degrees, which are themselves not very distinct from each other. It follows, therefore, that confusion and uncertainty must be found in the generative properties of the greater part of the effects to which I shall engage the attention, and that, on this subject, we are frequently reduced to point out some results of observation.

354. Nevertheless, the effects of the affinity which produces combinations, may also be perceived in the mutual action of substances which are submitted to the action of fire: thus the acids, which, notwithstanding their volatility, can resist the action of heat in the combinations which they form with earthy-alkaline substances, accelerate their fusion, and promote their vitrification; sulphate of lime, exposed to a great fire, runs into a transparent glass\*; sulphate of barites is reduced into glass, and also fluete of lime, in which the strong affinity of the acid can retain it, notwithstanding its own volatility.

\* Darcet. Mém. sur l'Action d'un Feu long-temps continué.

The effect of the acids must depend on the energy of their affinity, of their natural fixity, and of their peculiar fusibility: thus fluoric acid will produce a great effect by the force of affinity; phosphoric acid by its affinity and its fixity; and boracic acid by its fixity and its fusibility: the effect of the bases, which differ little in their fixity, will depend on their affinity and their natural fusibility; in the last respect, pot-ash and soda will be more powerful in this order of phenomena than lime: magnesia, which alone is very insoluble, will produce much less effect, notwithstanding the power of its affinity: it also abandons the greatest quantity of the volatile acids with which it was in combination; but I am convinced that it retains a part.

The combinations which will result from two substances, both of which can exercise a powerful action on the earths, and which by that means diminish the force of cohesion belonging to each, must be very proper to second the effects of heat on other substances; hence arises the utility of borate of soda, and the phosphates, in bringing other substances into their fusion.

If the results of all the experiments which have been attempted on the fusibility of insulated earthy substances are examined, it will be seen that lime and magnesia are the only ones which have given doubtful indications of fusion, either by the strong fire of furnaces, or by means of

lenses, or, finally, by the heat produced by the combustion of charcoal in oxygen gas: but by this latter means silex, alumine, and barites have been softened \*. This effect might be attributed to a portion of alkali arising from the charcoal, and exercising its action on these earths; but Hare, who employed the combustion of hydrogen gas by oxygen gas, says† that he has melted barites, alumine, and silex, on silver, as well as on charcoal; but that he could only obtain very doubtful signs of fusion with lime and magnesia; so that these two earths, and particularly magnesia, must be considered as the most infusible.

355. In the reciprocal action by which the term of their fusion is accelerated, the earths and alkalis show a power which has a marked similarity with the properties observed in them at common temperatures: silex does not exercise much action on alumine; but lime enters into fusion by the simple contact of the alumine in crucibles: this led Darcet, who first gave precision to the determination of the effects of a strong heat on mineral substances, alone or in mixture, to believe that this earth was fusible by itself, and served as a flux to the other earths. Pot-ash and soda, which have the property of dissolving silex and alumine, also promote their fusion to a degree which appears to be far superior to the

\* Essai d'un Art de Fusion, par Ehrman et Lavoisier.

† Memoir on the Supply, &c.

effect which could have proceeded from their own fusibility.

When the fusion is effected by means of the heat and the reciprocal action, the combination resumes the solid state; but the temperature must be inferior to that which was necessary to produce liquefaction, while each separate substance enjoyed its force of cohesion.

The combination, therefore, is maintained with the properties which result from the mutual action; the specific gravity will be less than that of the insulated substances, but the fusibility is much greater: the substances soluble in water have lost this property, and the force of cohesion is capable of resisting even the action of the acids on the alkalis of the vitrified combination, when they are not in too great a proportion.

The action of the alkalis on silex is employed to form glass; but to obtain some qualities in it, particularly that of being less brittle, lime is added to it, whose quantity is limited by its infusibility.

The more the heat is raised to which the vitrifiable mixture is submitted, the greater is the proportion of silex which can enter into the glass; but at a high temperature, pot-ash and soda volatilize: all that part which is not retained with sufficient force by the silex, is therefore disengaged, so that the proportion of the silex augments, and that of the alkali diminishes to the term of the equilibrium between the expansive force of the

the

the caloric on the alkali and on the silex, and the action of the silex, which tends to retain the alkali: the general laws of combinations are manifested in these effects.

To effect vitrification, vessels are necessary which can themselves resist the greatest heat, and also the action of the glass: alumine alone could fulfil the first condition, but it is soluble by the alkalis: it is true, that the action of the alkalis is partly exhausted on the silex, nevertheless the glass retains one sufficiently powerful: it can only be opposed by the force of cohesion which is procured to the alumine by desiccation and a strong heat, to which it has been previously submitted; nevertheless, a part of the crucibles liquefies, and enters into the composition of the glass: this effect can only be diminished.

The properties of glass, and all the conditions requisite for vitrification, are thus deduced from those of the substances which are employed to form it, and of the conditions which accompany the vitrification, as has been done by Loysel in an excellent treatise\*.

356. When glass is kept in fusion, it forms crystals at the bottom of the crucible, which have been observed by Keir; this crystallization has, without doubt, much resemblance to that which takes place in a liquid. It would be interesting to examine the proportions of the sub-

\* Essai sur l'Art de la Verrerie.



stances which compose these crystals, and to compare them with those of the glass from which they proceed, and which should form a more fusible combination than the symmetrical arrangement of the crystalline molecule may be effected in a liquid, as in that of salts.

When glass is cooled very slowly, there is also a separation of the least fusible substances, which do not take the crystalline form, or take it imperfectly, and which give a stony appearance to a matter which would have been maintained in the vitreous state by a more rapid cooling: hence the lavas, which were in the state of glass, lose this appearance by the slow cooling which they undergo, according to the observation of Hall. He has made another, not less interesting: it is, that after the separation, the substance, which, in part, is only in the state of a mixture, requires a much more elevated temperature than that which would have kept it in liquefaction in the state of glass. Kirwan explains\* this phenomenon very well, by the cohesion acquired by the least fusible substances, which separate, and, in this state, no longer exercise that reciprocal action on the other parts, which augmented the common fusibility in the state of glass: but he observes, that this effect must not be confounded with that of the evaporation experienced by the alkalis in glass, an evaporation which causes the

\* Observ. on the Proofs of the Huttonian Theory.

glass, that is kept long in fusion, to become harder; and it is known that the lavas also contain alkali.

If the preceding observations cannot lead to an exact explanation of the phenomena of vitrification, and of the properties which characterize the combination which forms, glass they can, however, indicate the causes, which I shall now resume.

357. When two solid bodies are exposed to heat, the reciprocal action of the parts which are in contact, concurs with the expansive action of the heat against the resistance of the cohesion of each of these two bodies: hence an infusible substance may serve as a flux to one which is equally so; the reciprocal action precedes the fusion and accelerates it, and, according to the circumstances, determines the proportions of the substances which liquefy.

The substances which, by the energy of their action, can produce a mutual saturation of their properties, have greater effects in vitrification than those which do not show this disposition, when their volatility does not prevent it, or when it can be subdued by the force which the combination produces.

The fusibility which they possess when insulated is another property favourable to the action which they exercise, and which may concur with the former.

In

In combinations which are in a state of saturation, the elements also act as soon as the heat has destroyed the effect of their mutual condensation, and then their natural fusibility can produce its effect.

The reciprocal action of the elements of these combinations is weakened by all that which the other substances present can exercise on them: hence it arises, that if one of these elements is volatile, it may be disengaged by a heat which, without this cause, it could have resisted: it is thus that sulphate of soda and sulphate of potash are decomposed in vitrification, and by that means their alkaline base is enabled to enter into the composition of glass. When the vitrified parts are sufficiently united to have but one common and resulting action, the glass is transparent; its particles do not exercise a separate action on the rays of light; it must be considered as a complete and uniform solution, as an homogeneous substance; but when, by the reduction of the temperature, the parts can separate and exercise an action which is peculiar to them, the glass acquires opacity and an earthly appearance: this effect arises from some substances being capable of having too great a force of cohesion, while others preserve the liquid state. This cause limits the quantity of lime which can be added to glasses composed of silex and alkali, and which, notwithstanding its alkaline properties, must not exceed 0.07 of the silex: if it exceeds this quantity,

tity, "although it is perfectly melted in the operation, the lime precipitates by cooling, it separates from the alkali, and the vitreous mass becomes opaque\*."

As the properties of substances become common, and nearly in a mean, in glass, the alkali in it loses its solubility, even in the acids, but the silex acquires a great fusibility: lime diminishes the fusibility; oxide of lead increases it.

358. Many aggregates or combinations are formed without the assistance of heat, which have a great correspondence with the products of vitrification; that is to say, in which simple substances contract a union which renders their properties common: the force of cohesion resulting from it is not only equal to that arising from the liquefaction, but it may be greatly superior to that of all the substances which have been vitrified. These combinations may also receive different proportions into their composition, according to the circumstances in which they are produced.

The combinations which are thus formed are not composed of earthy substances alone; they can also receive oxides into their composition, or aggregation; and when these are found in them in a certain quantity, they pass into the class of minerals. There is something arbitrary in this methodical separation; because it is not only the

\* Essai sur l'Art de la Verrerie.

proportions of the ingredients which are considered, but their importance with respect to their value or their utility in the arts.

If these aggregates or combinations have many characters in common with the products of liquefaction by the fire, they have also differences which must be attended to.

When the liquefaction is complete, the liquefied substance is in an uniform state; its properties result from those of all the substances which compose it; it is only by being cooled very slowly that it can form particular combinations, which then separate from those which retain the most fusibility.

In liquefaction, only that quantity of the volatile substances remains, which can be retained in combination at the degree of heat necessary to the fusion.

On the contrary, when an aggregate or compound is formed by a successive juxtaposition, several substances of different composition may be united in proportions, which vary according to the periods of their union: they can retain volatile substances, such as carbonic acid and water, in their composition, in greater quantities than if they had been exposed to the heat necessary to their liquefaction; they can also receive substances which, in the fire, could not retain the organic disposition found in them; finally, they sometimes form uniform and transparent compounds, but frequently they can only be considered



dered as a mixture of different substances, each of which exercises a reciprocal action with the adjoining substances, only at the surface by which they are in contact.

It is by these differences that mineral substances, arising from the action of fire, can be distinguished from those formed by juxtaposition; but when the liquefied substance has experienced a very slow cooling, it may have lost its homogeneity, as we have seen, and then it will be difficult to determine its origin.

359. Whatsoever may be the origin and formation of a mineral body, it may contain a certain proportion of a substance which, when alone, would have a great solubility, but which loses it by its combination with solid substances, whose insolubility it diminishes: thus pot-ash and soda enter into the composition of glass, which acquires a fusibility corresponding to the quantity which it contains. These alkalis are also found in the compound minerals which are formed either by the action of the fire, or by any other means. Kennedy found pot-ash in pumice-stone, and soda in basaltes; long since, Monnet obtained pot-ash from the aluminous earth of La Tolfa; Bergman and Vauquelin also found it there; and since alum can be obtained by treating the greatest part of the clays, carefully washed, with sulphuric acid, it may be concluded that it is usually combined with clay; Klaproth and Vauquelin found pot-ash in the leucite and  
in

in the lepidolite ; Vauquelin obtained it from the feldt-spar of Siberia ; and the proportion of these alkalis may be such, that Klaproth obtained 36 parts of soda from 100 of crysolite\* : now glass of a good quality should only contain 25 of alkali, and 75 of silex† ; nothing, therefore, can be ascertained from the nature of the substances found in minerals, with respect to their origin, unless these substances are volatile.

The force of cohesion may conceal the elements of a compound mineral, and their essential properties, that is to say, those which depend on the action which they can exercise, or on their tendencies to combination. Their aggregate, or their mutual combination, only offers the mechanical properties which depend on the cohesion, or on the gravity ; those which are derived from the more or less symmetrical arrangement which their molecu læ or their integrant particles can take ; and, finally, those which may depend on some accidents of little importance to the composition, such as the colours.

360. These qualities may, without doubt, be useful guides to recognize and class these minerals, but it is only the determination of the substances which compose them that can lead to a philosophical knowledge of their composition ; to that which embraces all the relations which

\* Klaproth. Beiträge, &c. Dritter Band.

† Essai sur l'Art de la Verrerie.

a simple or compound substance may have with all the other substances, and all the advantages which they may offer to the arts.

This application of chemistry to the knowledge of minerals has lately acquired great perfection from the scientific labours of Klaproth, Vauquelin, and several other chemists, who follow their footsteps with success.

In the mean time, if we consult the excellent summary of the analysis of stones, for which we are indebted to Vauquelin \*, we shall see that this analysis is simplified in proportion to its progress, as is the case with every branch of the sciences which advances in perfection, while the mineralogists, who were desirous of striking out a particular path for themselves, have strewed their science with difficulties.

To direct this analysis, the mineralogical characters of the substance to be submitted to it should be consulted, at first: but, without affixing more value to these indications, than they ought to have. Vauquelin says, “ hardness is not  
“ a property on which more dependance can be  
“ placed than on colour; the same substance en-  
“ joys many degrees of hardness, according to the  
“ circumstances which have accompanied its  
“ formation.....The specific gravity also leaves  
“ much uncertainty and want of accuracy, since  
“ it is very rare to find exactly the same weight

\* Ann. de Chim. Tom. XXX.

“ in the several varieties of the same body ; and  
 “ minerals of very different natures have fre-  
 “ quently gravities which are very similar..... Nei-  
 “ ther, in a great number of cases, is the crystal-  
 “ line form capable of showing the nature of mi-  
 “ nerals ; for many of them have a similar one,  
 “ or at least such as appears so to our senses : it  
 “ is thus that some celebrated mineralogists, by  
 “ taking this property for the basis of their sys-  
 “ tems, have united a multitude of substances  
 “ very different in their nature, and have sepa-  
 “ rated others perfectly homogeneous.”

If the substance to be submitted to analysis is a stone, it is prepared by reducing it to a powder by mechanical means : frequently this method is not sufficient to enable the chemical agents employed to separate the substances which were united.

Those substances, therefore, which oppose too much hardness to the agents of analysis are treated, by melting them with a considerable proportion of pot-ash or soda ; the compound which results, not only acquires much solubility, but the insulated combinations, which retained particular properties in their union, now form but one substance, in which all the elements exercise a reciprocal action, and yield to the different chemical effects by their solution in water.

If the force of cohesion is very considerable, it is possible that the action of pot-ash or soda may not be sufficient : thus Chenevix was unable to  
 liquefy

liquefy corundum, except by means of the borate of soda.

When by these means the obstacle of the force of cohesion is overcome, the processes to be employed are very analogous to those by which, after the example of Scheele (326), the distinction and separation of the different acids found in vegetable substances is effected. On the one hand, the acids which may exist in the substance to be analyzed are separated by means of the difference of solubility which their combinations with the alkaline bases possess ; on the other, different acids are employed to form combinations with the earthy or metallic bases: those which refuse to unite with these acids, in a given circumstance, are separated from those which experience solution ; these are afterwards distinguished from each other by the soluble or insoluble combinations which they can form with the different acids ; so that the solubility or insolubility of the uncombined substances, and of the different combinations which they yield, is the fundamental property which serves to guide the analyses of bodies which do not experience decomposition in the operations to which they are submitted. The difficulty is to separate the substances which have much similarity in the properties made use of ; and that which requires the most care in the analyst is to determine the proportions of the elements of the combinations which separate, or which form, with accuracy.

If



If the mineral contains an acid or a volatile substance, its analysis requires nothing particular in this respect.

Thus the same chemical means serve to ascertain the composition of substances which appear to be the most dissimilar in their properties : all the processes tend to separate their elements by the intervention of their elasticity, either natural, or increased by heat ; of their solubility ; and of their force of cohesion ; and by the assistance of the same properties which the combinations they form with the substances whose action is directed on them, receive.

## SECTION V.

*Of Metallic Substances.*

361. THE metals have properties which distinguish them from other substances, and which are so marked that no doubt can be raised as to those which should be placed in the class of metallic substances, except we have not yet succeeded in reducing them to the state of metal, and are consequently obliged to determine by the sole consideration of their compounds.

Their distinctive properties are principally derived from the reciprocal affinity by which they can combine with each other, while they unite with only a small number of other substances, from their specific gravity, which is much greater (that of tin, the lightest of metals, being 7.3, water being taken as unity, and the specific gravity of sulphate of barites is only 4.5); but principally from the affinity which they have for oxygen, and from the result of their oxidation, which also acquires properties distinct from those of other combinations.

The differences of these properties serve to compare them with each other; thus the specific gravity of platina is more than 20, while that of tin is

is only 7.3 : some can alloy in all quantities, and others can only unite in certain proportions : some have so strong an affinity with oxygen that it can hardly be separated from them ; others, on the contrary, have a very weak one : the oxides of all of them comport themselves in very different manners with the acids, and with the alkalis.

Among these properties, that which has most influence on their apparent qualities and on those made use of in the arts, is the force of cohesion, whose effects, combining with those of the figure of their molecularæ, occasion a difference in their pliability, their elasticity, their ductility, and their malleability, which seems to arise from “ the molecularæ having the faculty of yielding to pressure, “ by sliding over each other, so that the points “ by which they are attracted, although really “ displaced, are always at distances so small that “ the adherence continues \*.”

Finally, the metals differ from each other in the combinations which they can form with sulphur, phosphorus, and carbon.

The history of all the distinctive properties of metals forms a very extensive part of chemistry : I only purpose to compare their chemical action with that of other substances, and to indicate the causes of the particular phenomena which are owing to it.

\* *Traité de Minér. par Haüy. Tom. III. p. 348.*

## CHAP. I.

*Of the Reciprocal Action of Metals.*

362. Two obstacles oppose the action which the metals can exercise on other substances, as well as their reciprocal action, and diminish the effect of their affinity, their force of cohesion, and their specific gravity : we must examine their influence, and estimate their effects ; but since mercury remains liquid to  $38^{\circ}$  of the centigrade thermometer, below the freezing point of water, the first obstacle does not exist in respect of it : it is therefore by the consideration of the properties of mercury that the nature of this action, independently of the force of cohesion, whose effects we shall notice in the other metals, can be discovered.

Although mercury be perfectly liquid, it nevertheless has but a very weak tension at a common temperature : hence it can take the state of elastic vapour in a vacuum, and condenses in globules by a reduction of temperature ; but this effect is much less considerable than that of the greatest number of other liquids.

As is the case with the other liquids, an equal quantity of it will dissolve in a given space, at the same

same temperature, whether the space is a vacuum, or is filled with air more or less compressed (172); this explains the observation made by Monge and Vandermonde on the dissolution of mercury in atmospheric air\*.

Its tension increases with the temperature, and at 600° Fahr. can keep it in vapour, so that it is then equivalent to the weight of the atmosphere; since it augments proportionally with the temperature, it is seen that in the arts, when mercury and its amalgams are exposed to a high degree of heat, the air which is more or less heated can hold a considerable quantity in solution; nevertheless the solution of mercury by the air can only be compared, to a certain point, with that of the other liquids, on account of the more intimate combination which this metal can form with oxygen by oxidating.

This latter property principally distinguishes the metals which exercise an energetic action on oxygen: some of them, and particularly zinc, have a considerable tension, when the force of cohesion yields to the action of caloric, so that they are abundantly volatilized, as soon as they are in fusion; but this tension does not produce the effect of solution by contact of the air, because an intimate combination with the oxygen succeeds, or even precedes the entire liquefaction; so that the principle that a substance which has become

\* *Mém de l' Acad.* 1786. p. 436.



gazeous is found in equal quantity, at the same temperature, in a space which is a vacuum or filled with air, is not applicable to this circumstance.

No solution in the air is therefore perceptible, except in those metals which have only a weak action on oxygen: thus, according to the observation of Macquer, gold placed in the focus of a powerful burning glass is reduced into a vapour, which gilds plates of silver exposed to this exhalation.

If, at a low temperature, the tension of mercury is very inferior to that of the other liquids, it appears that this difference depends, in a great measure, on its specific gravity, which is a force opposed to elasticity, and which concurs with the force of cohesion; for the most evaporable liquids are generally the lightest: the elastic tension, on the one part, and the specific gravity and force of cohesion, on the other, may be considered as opposite forces. Nevertheless, the specific gravity must not be considered as the only cause of the difference of the tension of metals in fusion, or even of other liquids; but whatsoever may be the principle of this property, it must not be distinguished from the force of cohesion, or the reciprocal action of the *moleculæ* which expresses all its effects.

Thus, by its specific gravity, mercury retains some of the attributes of the force of cohesion, notwithstanding its liquidity; the mutual action of its *moleculæ* will produce greater effects than that of more evaporable liquids; it will therefore be more easily reduced into globules, and these will be blended by their mutual action; but this  
property

property is destroyed by the affinity of a metal which can incorporate with the mercury ; it diminishes in proportion as the temperature becomes more elevated, and augments its tension.

363. Some phenomena prove that mercury exercises an action on a certain number of substances, stronger than the mutual action of its *moleculæ* ; for example, it appears to hold a little water in solution, although Boerhaave could not discover any by a change in the weight ; but what he employed was probably already saturated with water : iron which is kept immersed in mercury becomes oxidized, which it could not do except by means of the water which it decomposes ; it adheres to the glass of a barometer, and acquires a flat surface when the water which it might contain, and that which might adhere to the glass, are carefully driven off ; by using the same precautions to expel the water from a capillary tube, it attains its level in it\*.

Nevertheless, the action of mercury is only shown in a weak degree, and on a small number of non-metallic substances, with the exception of oxygen, sulphur, and phosphorus ; the other metals give still weaker indications ; Rumford found that plates of gilt silver did not acquire any weight by keeping them in the most humid air, while every other substance which he submitted to the same trial acquired more or less †. This property

\* *Seances des Ecoles Normales*. Tom. III. p. 50.

† *Philos. Trans.* 1787.

of exercising a stronger or weaker mutual action, and of being inactive with the greater part of the other substances, must, therefore, be considered as an attribute which distinguishes the metals: nevertheless, at a high temperature the fluxes accelerate the term of the liquefaction of metals, which shows that they then exercise an efficacious action on them.

364. Mercury dilates much more in an equal number of degrees of the thermometer than the solid metals: while it passes from congelation to the liquid state an alcoholic thermometer remains at the same degree: Cavendish found that the thermometer was also stationary during the liquefaction of lead and tin \*. It cannot, therefore, be doubted that caloric follows the same laws with the metals as with other bodies in respect of their being solid or liquid, and of their passage from one state to the other. The property which they have of absorbing caloric by liquefying, proves that the force of cohesion is an obstacle to the combination of caloric (107), whence it may be concluded that the metals must experience the effect of caloric, that is to say, must dilate, in proportion as their force of cohesion diminishes, or they approach the state of liquefaction; and when they are in the liquid state, their dilatation by equal quantities of caloric will be also greater as they are nearer to the term of their ebullition, as is observed in all other liquids (104).

\* Observ. on Mr. Hutchins's Exper. Philos. Trans. 1783.

As among the other liquids which pass to the solid state there are some which undergo a contraction, and others which dilate, there are also metals which contract, and others which experience an expansion: mercury is in the number of the first, and, from an experiment of Brown, Cavendish estimates its condensation at  $\frac{1}{23}$  of its volume.

Reaumur noticed this difference between the metals long since\*, he observed that cast-iron dilated by cooling, so that its surface became rounded by this effect, while that of the metals which contract became concave: in consequence the melted iron filled the moulds into which it was poured, and took an exact impression, while that taken by the other metals experienced a contraction.

This great observer compares this expansion to that of water which congeals; he observes that it precedes the moment of congelation in the melted metal, as well as in water; both commence by dilating quietly, and the effect becomes greater when they approach congelation; so that then jets are thrown from their surface.

He submitted the different metals known in his time to experiments by fusion, and examined particularly if the solid metal rose above the liquid part with which he covered it, to distinguish those which experienced a contraction in passing to the

\* Mém. de l'Acad. 1726,

solid state, from those which dilated, and he found that cast-iron, bismuth, and, with some uncertainty, antimony, were the only ones which had the property of dilating; but the contraction of the others was not alike in all.

Finally, sulphur, tallow, wax gave a greater specific gravity in the solid state than in the liquid state, which proves that the contraction of substances which pass to the solid state is the general phenomenon, and that the dilatation is an exception, but that it does not belong to water alone, and cannot be attributed to any other cause but the arrangement which the *moleculæ* take when they pass to the solid state, and which had been noticed before by Reaumur.

365. If the passage from the liquid to the solid state is tranquil, the *moleculæ* of the metals can take a symmetrical arrangement, and they crystallize; but although they differ from each other in the disposition to crystallize, the forms of the crystals vary but little; and whether this crystallization can be effected, or the form of the *moleculæ*, and the relations of their positions can be altered by compression, the distinctive properties of each metal, those which depend on its chemical action, remain untouched; no other changes are perceived except those which must arise from the greater approximation of the *moleculæ*.

The effects, therefore, which seem to depend on the form and arrangement of their *moleculæ*, only relate



relate to the crystallization, and to some modifications of the reciprocal action, in so far as it produces hardness, pliability, brittleness, and ductility : hence also arise the differences observed in these properties when metals are exposed to the action of heat ; the malleability and ductility of some augment, and others become more brittle ; this consideration may be applied to the state of mercury which has experienced congelation ; flexibility and malleability have been found in it ; but no conclusion can be formed from the qualities it offers in this respect, in a state so near its liquefaction, with respect to those it would have, if it were at a great distance from this state.

366. The action which mercury exercises on the other metals and consequently its comparative affinity for them, might be measured by the quantity which it would dissolve of each of them if they resisted it with an equal cohesion ; but they differ greatly from each other in this respect : it is, nevertheless, seen that there is also a great difference which is independent of the force of cohesion, for it easily dissolves gold, which has a great tenacity, in the cold, while it cannot combine with iron and cobalt, and only dissolves some other metals with difficulty. Silver is one of those which have the most affinity with it, and by the condensation which its combination experiences it becomes heavier than the mercury itself.

The

The same effects are observed in this solution of the metals as in those which are effected by the other solvents (16): at first the solid metal takes the mercury until the force of cohesion is sufficiently destroyed to enable the latter afterwards to effect its solution and render it liquid, and before entering into solution the first becomes so much the more brittle, as it takes a greater quantity of mercury.

The solution is more rapid and easy, as the quantity of the solvent is more considerable: heat favours this combination by the diminution which it produces in the force of cohesion of the solid metal; it is even necessary to some amalgams: but if the heat is too great, it becomes injurious by the volatility it gives to the mercury, and by increasing this volatility to a certain point, it separates it from all its combinations with the other metals.

In promoting amalgamation, the heat also acts by the motion which it introduces on account of the inequalities of the temperature; this action is assisted by trituration, which brings the least saturated parts of the liquid to the solid metal.

Like the other solvents, mercury facilitates the combination of the metals with other substances which, before, could not act in a sufficient mass to overcome the force of cohesion; so that the metals which are reduced into an amalgam, and which have a greater affinity for oxygen than the mercury,

mercury, which has destroyed their force of cohesion, are more easily oxidized than in their insulated state.

The combinations of mercury with the metals tend to assume a crystalline form, and there are some which actually crystallize when they are left undisturbed, as is observed in the amalgam of tin: this effect is analogous to that of the crystallization of salts in water: one part of the metal held in solution remains in the liquid, while another part crystallizes with another quantity of mercury which is determined by the force of cohesion belonging to the combination: a division of the solid metal takes place, and two combinations are formed, one of which has an excess of this metal, and becomes solid, the other with an excess of mercury remains liquid.

Since these amalgams have generally a consistence which opposes this effect, it is more easily produced by keeping the solution at an elevated degree of heat, and by employing a great proportion of mercury: it is thus that Sage effected the crystallization of several amalgams, and he observed that the crystallization of the greater part of them, and even that of silver, took place at the surface of the liquid, although the amalgam of silver was become heavier than the mercury itself; but that of gold crystallizes at the bottom: the first effect is explained by the greater proportion of solid metal which enters into the formation of the crystals, and which, being lighter than the mercury, will

will give more lightness to the part which crystallizes than to that which remains liquid, and in which the heaviest predominates, so that the specific gravity of the amalgam varies according to the proportions: gold being the heaviest, the contrary effect will take place. The figure of these crystals is not that peculiar to each metal, but belongs to the combination.

These amalgams have so much the more liquidity as the proportion of mercury is greater in them, and when this is driven off by heat, it requires a more elevated degree as its proportion diminishes: finally, the specific gravity of most of the amalgams, and perhaps of all of them, is greater than that of the metal and of the mercury taken separately.

367. The alloys offer analogous properties, with the exception of those which depend on the liquidity, at an ordinary temperature; so that the amalgams are alloys of a metal, naturally liquid, with the solid metals.

No effect is perceived in these combinations of the metals with each other similar to that observed in combinations in which the opposing properties are saturated: on the contrary, a distribution of properties is made in the ratio of those possessed by the elements, and of the quantities which unite: an alloy may be said to be an intermediate metal, with the modifications dependent on the reciprocal action of its moleculæ, but it retains all the distinguishing qualities of the metals.

The

The action which the metals exercise on each other is varied by the affinity, and by the relations of fusibility and specific gravity; so that, the affinity being equal, the metals are less disposed to alloy as they differ more in their fusibility and in their specific gravity, and when their affinity is not great the distance of their fusibility may be a sufficient obstacle to prevent their union: thus iron, which solders and unites easily with copper, and which in that respect, shows a sufficiently energetic affinity for it, nevertheless, can only alloy with this metal in a very small proportion, by means of fusion.

In general, the alloys have more hardness than the metals of which they are composed, which is a consequence of the contraction they experience; but this quality varies according to the proportion: by augmenting that of the most ductile metal, the alloy itself becomes softer, and, on the contrary, it becomes harder and more brittle by a greater proportion of the hardest metal: it is the same with the other qualities which each metal, in a more or less perceptible manner, communicates to the alloy, in the composition into which it enters.

On the contrary, the alloys have a greater fusibility than that which should result from the fusibility of the metals taken separately: this effect also results from the reciprocal action which they exercise, similar to that observed is the mutual action of the alkalis and the earths; and, as



is the case in the earths, the action of three metals sometimes produces a greater effect than that of two ; it is thus that the alloy, for the knowledge of which we are indebted to Darcet, and which is composed of eight parts of bismuth, five of lead, and three of tin, acquires such a fusibility that it becomes liquid at a temperature below that of boiling water : this proves that the metals exercise a mutual action which determines their liquefaction, even while they are in the solid state, since at this temperature each of the metals is still far distant from entering into liquefaction by itself ; an effect which is also similar to that observed in the mixture of the infusible earths with each other (357).

This effect of the mutual action of metals is also observed in the amalgams : bismuth has the property of forming a liquid amalgam which passes through chamois leather : that of lead has much less liquidity ; but if it is mixed with the first, that which it acquires admits of its passing through the leather.

Bismuth exercises the same action on the other metals, particularly in the amalgam which it produces in common with tin, and this is employed to silver glass balls which cannot be subjected to the usual process of silvering.

Nevertheless, if the affinity of the metals which form an alloy is not also considerable, they retain so much difference of fusibility that the most fusible enters into liquefaction before the other, when they are submitted to a graduated heat, and the  
greatest

greatest part of it may even run off before the other begins to enter into fusion ; and if the alloy is composed of three metals, the most fusible can carry with it that one of the two others for which it has the most affinity, or whose fusibility differs least from its own.

On this property is founded an operation in metallurgy which is called liquefaction, and in which silver is separated from copper by the intervention of lead. To produce this separation, a certain quantity of lead is added to the copper which holds the silver, and this ternary alloy is flattened ; it is then exposed to a heat which is just sufficient to melt the lead which carries the silver with it : if there is any gold in the alloy, it remains united with the copper, while the silver alone runs off with the lead : but as the action is modified by the proportions, when that of the silver is considerable, this metal is divided between the copper and the lead ; if, on the contrary, the proportion of the lead is too great, its action becomes too powerful, and liquefies a portion of the copper.

For the same reason that alloying accelerates liquefaction, it promotes the oxidation which was opposed by the force of cohesion, as we have observed that the metals dissolved in mercury are much more easily oxidated than when they possess their force of cohesion ; but this effect precedes the actual liquefaction, and takes place as soon as the force of cohesion is sufficiently diminished ;

Proust says\*, “when platina is combined with the other metals, it oxidates more easily than has hitherto been believed. Platina, therefore, has this property, like the other metals, in which a state of combination always favours oxidation.”

368. When the affinity of one metal for another is not sufficiently powerful, in all the proportions, to overcome the obstacles opposed by the mutual affinity of the particles of each metal, the difference of fusibility, and that of the specific gravity, a division is then made, such as we have seen is produced by the difference of solubility in the reciprocal action of the acids and alkalis (62-69). The lightest metal forms one alloy in which it predominates, and which is placed above another alloy, holding the heaviest metal in the greatest proportion. Bergman has analyzed this phenomenon in the mixture of iron and tin†. If equal parts of iron and tin are melted, two alloys form, of which the superior is composed of one part of tin, and of  $\frac{1}{2}$  of iron, and the inferior contains one part of iron and half a part of tin; if, therefore, a mixture is liquefied in which the tin does not exceed the half of the iron, only one alloy is formed, and one only is also formed when the iron is only  $\frac{1}{2}$  the weight of the tin: in the first, the properties of the iron predominate; in the second, those of the tin: the intermediate quantities to those described produce the two alloys, whose relations vary according to the quantities.

\* Ann. de Chim. Tom. XXXVIII.

† Bergman. *de ferro et stann. igne commix.*

Bergman's theory is applicable to the other metals which separate by forming two masses, whose proportions are determined by the respective specific gravities and fusibilities.

According to Guyton\*, these two alloys are observed with inverse proportions in the fusion of silver, and in that of lead, with iron.

When equal parts of lead and zinc are fused, two alloys also form, according to the observation of Baumé: I have ascertained that the upper contained lead, and the lower zinc.

Cobalt and silver also separate into two ingots, in each of which the existence of the two metals may be discovered by the colour alone, according to Gellert.

The same chemist observed that when cobalt and lead were melted together, the cooled mass separated into two; whence he concluded that these two metals did not unite: but Wasserberg observes† that if the cobalt is afterwards melted with iron, lead precipitates.

Nickel and silver also give two separate masses, which, it has been asserted, were each formed of one metal without mixture: it is probable that they had not been submitted to a rigorous examination, and that the double alloy is a general phenomenon of metals, which do not unite in all quantities; but that the proportions will vary in the different metals.

\* Ann. de Chim. Tom. XLIII.

† Instit. Chim. Tom. I. p. 395.

The difference of the specific gravity is sufficient to establish a variation in the proportions of alloys, even in those in which it does not occasion a separation on cooling, so that if the liquid metal is left long undisturbed, a greater proportion of the heaviest metal will be found at the bottom: this shows the necessity of mixing alloys carefully to obtain them in a uniform state.

Almost all the alloys have a greater specific gravity than the metals which compose them taken separately; this difference is sometimes considerable: Borda observed that the specific gravity of brass was nearly a tenth greater than that of the two metals which form it; there are, however, some exceptions: copper and silver have a lower specific gravity when they are alloyed than when insulated; it is the same with the alloy of gold and tin, with that of gold and iron, and with that of bismuth and iron. This increase of volume must be attributed to the same cause as that observed in ice and in some amalgams.

All the properties which we have just examined in the metals prove that they exercise a mutual action, similar to that of other substances which in their combination do not sensibly produce a saturation of the opposing properties, but which take a medium between those which each possesses, according to their energy, and according to their respective quantity: it is only the properties dependent on the reciprocal action of the molecules, which receive an alteration, caused by the approximation



mation of these moleculæ, or by the form which they take: the action of caloric concurs with the reciprocal affinity of the metals, to destroy the effects of the cohesion which, at first, had acquired an increase by the condensation arising from this affinity.

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## CHAP. II.

### *Of the Oxides.*

369. THE predominant character of metallic substances is their inflammability, or the affinity which they have for oxygen: all the other combinations which they are capable of forming yield to this affinity unless the force of cohesion has sufficient energy to support them. I shall now examine this property and its results, by comparing the metals, in this respect, with the other simple bodies which possess it, and by endeavouring to find, in their primitive dispositions, the reason of the phenomena which they offer in their oxidation.

The oxidation of the metals, and the properties of the oxides which they form, depend on the strength of their affinity for oxygen, on their force of cohesion, on their fusibility, on their volatility, on the degrees of oxidation which they can attain in proportion to these qualities, on the condensation

tion which the oxygen experiences in them, and on the quantity of the caloric which it retains.

The metals differ considerably in the affinity which they show for oxygen: gold, silver, and platina cannot commonly combine with it, except by the intervention of an acid, which, by its action, seconds that of the oxygen, which must be in a state of condensation: it seems, however, that this difficulty of combining with the oxygen, in an elastic state, arises only from the force of cohesion of these metals, which require a high degree of temperature to take the liquid state: now this elevated temperature increases the elastic effort of the oxygen gas proportionally, and consequently augments the obstacle to its fixation; for silver, and even gold, when they lose their coherence by forming a liquid amalgam with mercury, are capable of being oxidated at the temperature of the atmosphere.

It may be objected to what has been just said, that gold and silver are vitrified when they are exposed to the strong heat of burning glasses\*; but by attending to the description which has been given of this effect, it will be manifestly seen that it was the action of some parts of the support which occasioned the vitrification of these metals, as it is the action of an acid which determines their oxidation and solution, since the colour of the vitrified part varied according to the nature of the

\* Macquer, Dict. de Chim. au mot *verre ardent*.

support;

support; and since the latter vitrified at the part which held the metal, and formed a glass coloured by its oxide.

In fact, the oxides of these metals which can only be formed by a concurrence of causes, easily resume the metallic state, when they are exposed to the action of heat, and cease to be protected by a resulting affinity: it cannot be supposed that this action, by being rendered more energetic, can produce an effect totally opposite.

This is applicable to the vitrification which Macquer observed was effected on the surface of globules of silver enclosed in balls of porcelain paste: the combustion which the diamond and other combustible substances experience in vessels of porcelain closed with the greatest care, when they are exposed to a very elevated temperature, shows that this substance is not, in this circumstance, a security against the access of oxygen: the silver was therefore subjected to the combined action of the oxygen and the porcelain: it was in the same situation as an oxide of silver, which, when combined with the earths, resists a high degree of heat: the effect might depend on the water retained in the alumine, but the explanation would be the same.

370. Since the force of cohesion is an obstacle to oxidation, the metals must resist the action of the oxygen in proportion to their hardness, and the elevation of temperature will intervene in proportion to their fusibility, supposing their affinity to

to be the same; thus some metals which have a strong affinity for oxygen, such as zinc and tin, remain without oxidation, or contract a very slight one on their surface, when they are left exposed to the atmosphere; but they oxidate as soon as they become liquid, or even when they approach the liquid state, and their force of cohesion is sufficiently weakened.

Although mercury seems to have an affinity for oxygen but little different from that of gold and of silver, it nevertheless oxidates at a certain temperature; that which is near to its own ebullition seems most suitable to this effect: if it had not the property of vaporizing at a temperature but little elevated, it would not combine with oxygen more easily than gold or silver; since when it is oxidated it abandons the oxygen at a temperature which is only a little higher than that at which the oxidation was effected, and since, in the supposition of a more considerable force of cohesion, it would require a heat superior to that in which it could remain an oxide, to destroy the obstacle.

If, therefore, gold and silver do not oxidate by the sole action of heat, it is only because they require a more elevated temperature to liquefy, than that at which the oxide of mercury could exist. This proves that even that force of cohesion which the mercury still retains in the liquid state, and whose effects must be blended with those of the specific gravity, is an obstacle to its combination with oxygen: it is only by keeping it strongly agitated in atmospheric

pheric air, or in water, that we can succeed in producing a commencement of oxidation in which it takes the form of a black powder, but it cannot go beyond this first term, so that it must be reduced into the vaporous state to enable it to form the red oxide: we shall presently see what influence this state can have on its degree of oxidation.

371. Another property which modifies the results of the affinity of the metals for oxygen, and of the resistance of the force of cohesion, is the volatility which they acquire by heat.

A metal which volatilizes as soon as it enters into liquefaction, such as zinc, is quickly in the state most favourable for the combination (206); it will therefore immediately combine with a determinate proportion of oxygen, with that proportion in which the reciprocal action produces the greatest condensation; then the ulterior action of the oxygen gas cannot surmount the obstacle which the condensation opposes to it, as we have noticed in the formation of sulphureous and phosphoreous acid which cannot pass to the state of sulphuric and phosphoric acid except under other conditions, and in the production of water which receives constant proportions of hydrogen and oxygen at once. If the oxides which are thus formed are exposed to a superior heat, the fixity which they have acquired occasions the oxygen to be disengaged from them, which proves that the heat only contributes to the oxidation because it destroys the resistance of the cohesion.

The



The preceding observations are applicable to the oxidation of mercury, and explain the two degrees of oxidation to which it is limited. The reciprocal action of its particles opposes its combination with oxygen; if this is diminished by mechanical means, it passes to a state of oxidation which may be compared to the oxygenation of sulphur which forms sulphureous acid: to produce a more intimate combination, it is necessary that it should be reduced into a dense vapour; then it is in solution in atmospheric air, and the two elastic fluids, which exercise a mutual action, enter into combination in the proportions which produce the greatest condensation: in proportion to this condensation the oxide which is formed precipitates, and its moleculeæ collect like those of a saline substance which crystallizes in a liquid, or of a liquid, which, by a reduction of temperature, passes slowly to the solid state.

372. This condensation of a metal and oxygen is not an hypothesis, but is proved by the fixity of the oxide which is a consequence of it: thus the oxide of mercury is less volatile than the metal: zinc, which is volatile at a degree of heat but little elevated, forms an oxide which resists the greatest degree of heat without being volatilized: the oxide of antimony is much less volatile than the metal: the oxide of arsenic is less so than arsenic, although these oxides have received an element into their composition naturally very elastic: but all the effect of the tension of the oxygen and of that

that of the metal is destroyed by the force of the affinity, and it is only when this tension has taken a sufficient intensity that a more or less considerable part of the oxygen can disengage in gas.

It is evident, therefore, that the oxides will attain a term of oxidation which they cannot exceed in common circumstances, that is to say, when the affinity of the oxygen is not assisted by some circumstance favourable to its action, and that they must more particularly reach this term when their volatilization permits them to exercise an action on the oxygen which is not counteracted by the force of cohesion and by the specific gravity.

373. Some chemists, struck with the fixed terms to which some oxidations are limited, suppose that there is always determinate degrees to which the combination of oxygen is subjected: they give nature a balance, which, subjected to their decrees, determines the proportions of combinations, without any attention to the circumstances in which the causes may be found which limit the action of substances having a tendency to combine, and of whose influence it is important to theory to form an estimate.

A chemist whose opinions have great weight, Proust, has particularly endeavoured to establish this doctrine, supporting it by several new and interesting facts: as the explanations I offer are founded on a different hypothesis, I think it right to give his opinion in his own words.

“These

“ These proportions always invariable, these  
“ constant attributes which characterise the true  
“ compounds of art or those of nature, in one  
“ word, this *pondus naturæ*, so well observed by  
“ Stahl ; all this, I say, is no more in the power of  
“ the chemist than the law of election which  
“ governs all combinations\*.”

Proust, therefore, applies a principle to the oxides which he considers as general : he admits an elective affinity in substances, and he considers the proportions which form each combination as fixed by an invariable law. I shall not resume the discussions into which I have entered with respect to other combinations, but it will be manifest that the consequences which I have drawn from the chemical action of other substances will receive a new confirmation from the properties of the oxides, and thus acquire more generality.

I must, therefore, show that the proportions of oxygen in the oxides depend on the same conditions as those which enter into the other combinations ; that these proportions can vary, progressively, from the term at which the combination becomes possible, to that at which it acquires the highest degree ; and, that when this effect does not take place, it is only because the conditions which I have pointed out become an obstacle to this progressive action : I shall begin by offer-

\* Ann. de Chim. Tom. XXXII. p. 31.

ing proofs of my opinion which shall be developed in the following chapters.

374. If the metals which oxidate by volatilizing take at once those proportions of oxygen which may be considered as constant, and if the determinate proportions of oxygen they receive, seem to favour the opinion against which I protest, this is not the case with those which enter into a tranquil fusion, like tin and lead : their oxidation advances from the lowest degree to a term, which, however, is not the extreme of the oxidation they may receive in other circumstances, and the succession of colours, and of the other properties which accompany each degree of oxidation, is observed : thus lead forms an oxide which begins by being grey ; afterwards it passes to different shades of yellow, and finishes by becoming red, by means of a circumstance which shall be discussed : iron also passes through different shades, and acquires different properties in proportion as the oxidation advances : similar effects may be observed in several metals.

If, therefore, some metals, by a certain temperature, acquire a degree of oxidation in which the proportions of oxygen seem to be fixed, it is only because the conditions of the oxidation are then the same, and all the combinations produced under the same conditions must be uniform : now, it is chiefly when the oxidation is effected at the moment when the elastic tension of the metals volatilizes them, that the conditions of the oxidation are principally found

found to be determinate; but whether the metal possesses the property of volatilizing, or whether it oxidates more unequally by successive degrees of heat, it is easy to discover that the combination of the oxygen with it can vary, and that even indefinitely, from the period when, by the force of cohesion losing its preponderance, the oxidation becomes possible, to the extreme at which it ceases, unless the mutual affinity of the two elements is assisted by some other affinity which carries the term of oxidation farther.

If the oxides, which are become fixed by the condensation produced, are subjected to a degree of heat superior to that which occasioned their oxidation, they abandon part of their oxygen, and remain in another state.

Thus the oxide of antimony obtained by sublimation, contains, according to Thenard\*, 20 parts of oxygen in 100: this oxide exposed to a gradual heat gave him four other degrees of oxidation which contained from 16 to 20 parts of oxygen: although such of these results as only differed a few hundredth parts from each other cannot be considered as rigorously precise, the qualities shown by the oxides do not admit of a doubt that the proportions of oxygen were really different. The same chemist concludes from the interesting experiments which he has made on cobalt that there exists at least four species of

\* Ann. de Chim. Tom. XXXII.



oxide of cobalt; the blue oxide, the olive oxide, the dark brown (*puce*) oxide, and the black oxide, which have different proportions of oxygen.

Clement and Desorme found that the sublimed oxide of zinc contained nearly 0.18 of oxygen; but having urged it by a strong heat, it took a yellow colour, and they only estimated that which it retained at 0.1164\*. They add, with reason, that it is probable that by heating the white oxide more strongly, it might be made to lose still more oxygen. It is to be observed, that, according to Vauquelin, whose accuracy is known, the oxide of sulphate and of nitrate of zinc contains 0.31†.

This disoxidation by the force of heat is particularly observed in the oxides which are formed without the volatilization of the metal, and which acquire different degrees of oxidation with more facility: in all of them there is a term in the temperature which is most favourable to the combination with the greatest quantity of oxygen; beyond this term they lose a greater or less portion of the oxygen by heat, according to the temperature, and according to the force with which they retain it.

When the red oxide of lead is exposed to a strong heat, part of the oxygen is driven off, and it is brought to the state of yellow oxide; the oxide of lead could not, therefore, have acquired the proportion of oxygen which gives it the red colour, if

\* Ann. de Chim. Tom. XLII.

† *Ibid.* Tom. XXVIII.

it was kept at the degree of heat which it requires, or which it can, at least, support, in taking the yellow shade ; so that by exposing the red oxide to this same heat, it returns to the yellow colour by abandoning the portion of oxygen which makes the difference of the two oxides : this explains why, in the fabrication of minium it is finished by keeping the oxide some time at a more moderate heat than that which it had previously supported, and that for this purpose, the communication with the air necessary for the support of the fire, is intercepted.

The oxide of manganese exposed to the action of the fire abandons a proportion of the oxygen so much the greater as the heat is more elevated, and by this means it may be brought near to the state of white oxide ; but the heat must be progressively augmented, so that that which can disengage one part may not be sufficient to volatilize that which succeeds it : if the black oxide was only a mixture of the most oxidized metal with that which is least so, as it must be supposed in the opinion which I discuss, and if there were no intermediate degrees of oxidation, the same temperature would be sufficient to make all the oxide pass from one state to the other ; but observation proves that, conformably with the other combinations, the oxide opposes a resistance, increasing as the quantity of oxygen diminishes.

It is the same with the oxide of iron ; for if the red oxide is exposed to the action of the fire, it gradually

gradually assumes a purple colour which becomes deeper and deeper, and thus it approaches to the black oxide.

For the same reason, when the oxidation of iron is effected by a very high degree of heat, it is not the red oxide which forms, but a black oxide. The scales which are detached from forged iron, and which have been employed by Priestley in several experiments, under the name of *finery cinder*, are in this state.

375. If the action of any substance seconds that of the heat, the oxide abandons its oxygen more easily, at least as far as the point corresponding to the combination which forms: when, on the contrary, this substance can combine with the oxide, it maintains the degree of oxidation by all the force of the combination which it can form with it, until the expansion which the oxygen tends to take, overcomes this effect.

For example, the oxide of gold and that of silver are capable of melting with vitrifiable substances which enter into combination with them; they then sustain a degree of heat far superior to that which would have been sufficient to reduce these metals: hence it arises that the oxide of silver which enters into vitrification with the earth which it dissolves in a crucible of clay, cannot be reduced, according to the observation of Sage\*, except by the intervention of inflammable substances.

\* Mém. de l'Acad. des Sciences, 1786.

The substances which have thus the property of combining with the oxides also promote the oxidation of the metals, as we have seen with gold and silver which had been exposed to a strong heat on a support, capable of entering into vitrification with their oxides (369). It is thus that a cupel made of phosphate of lime, favours the formation of the oxides with which it can enter into combination, and not, as has been believed, because it can lodge the liquefied oxides in its interstices.

In this property of the resulting affinity is found the reason of the different effects which the acids and the alkalis produce on the oxides and on the metals: in general, the acids have a stronger action on the metals which are but little oxidized, than on those which are much so; they also favour the disengagement of oxygen as far as the term of the oxidation which suits their combination: the sulphuric acid drives off that portion of oxygen which constitutes the difference between the black and the white oxides of manganese, at a heat, much below that which would have been necessary to produce its disengagement if heat alone had been employed.

The alkalis, on the contrary, which seem to have a stronger disposition to unite with the metals when greatly oxidized, retard the disengagement of oxygen by heat: I have melted pot-ash with the black oxide of manganese, which forms the combination described by Scheele, and remarkable for

for the variations of colour which its solution undergoes : it required a heat which would have been sufficient to have driven off a part of the oxygen from the oxide alone, but none was disengaged : the red oxide of lead is also capable of being melted with an alkali, without a disengagement of oxygen gas.

376. A substance may also change the state of the oxide by the action which it exercises on the oxygen alone : thus the red oxide of mercury, ground with mercury, shares its oxygen with an indefinite quantity of the latter, and forms an oxide which varies according to the proportions, and which takes different shades of greyish yellow : by heating equal parts of iron-filings and red oxide of iron, Vauquelin obtained, without any gas being disengaged, a total of black oxide which had no more than 0.25 of oxygen\*, while the red oxide had previously contained from 0.40 to 0.49 ; but there can be no doubt that by varying the proportions, oxides will be obtained in this manner, in which the oxygen will be found in very different proportions from those of the black oxide : an experiment of Chenevix proves, that, by a similar method, an oxide may be reduced much below the term of oxidation which has been considered as its *minimum*. He produced an oxide of copper which contained only  $11\frac{1}{2}$  per cent. of oxygen, by melting an oxide which contained 20. with the same

\* Syst. des Conn. Chim. Tom. VI. p. 161.



metal\*. The colour of this oxide is very near that of the copper; he preserved it by using great precaution in introducing it into enamels, to which it gives a shade which is in great request, but very difficult to obtain.

This action, which substances exercise on oxygen also, forms combinations which separate, and thus the metals are brought back to different degrees of oxidation, and to their entire reduction, by a heat considerably less than that which would have produced this effect alone: I have brought the white oxide of zinc to the state of yellow oxide by passing a current of hydrogen gas over it in a red-hot tube, but at a much lower heat than would have been required for this result without the hydrogen: on this depend the effects of the decomposition of ammonia by the oxides. Thenard observed that antimony, precipitated from its solutions by iron and zinc, was of a black colour, and contained only 0.02 of oxygen.

377. That which proves that caloric is only favourable to oxidation as a force opposed to cohesion (209), and that it becomes an obstacle to a more advanced oxidation, is, that when the extreme degree of oxidation which can be procured by the most suitable temperature is attained, it is still very distant, in several metals, from that which can be obtained by bringing oxygen into action, when it is condensed and

\* Philos. Trans. 1802.

weakly retained in another combination: thus more oxygen is given to the red oxide of lead, by means of oxygenated muriatic acid and of nitric acid, as had been noticed by Scheele, and as has been particularly shown by Proust: by this means the oxide acquires a brown colour, and it easily abandons the excess of oxygen which it had received by heat. Chenevix seems to have produced a similar super-oxidation also in the oxide of mercury. Thenard has remarked that antimony, which by the action of fire could only take 0.20 of oxygen, might receive as much as 0.32 by similar means. The oxide of arsenic is converted into an acid, in the same circumstances, by combining with a new quantity of oxygen.

The effects which I have attributed to the greater condensation produced by the reciprocal action of oxygen and a metal, in determinate proportions, disappear before the action of heat, which destroys them by dilatation, as is observed in the decomposition of nitrate of pot-ash, and in all similar circumstances (184): then the last portion of oxygen, which increased the condensation, yields to the expansive action, and the oxygen is only retained in proportion to the quantity of the metal which acts upon it; so that the required force of heat must increase as the quantity of oxygen diminishes: if this effect is not observed in the reduction of mercury, it is because this metal is very volatile, and the expansion which it acquires is prejudicial to the action which it exercises on the oxygen.

It

It has been thought that the metals which were greatly oxidized were much more difficult to reduce than when they were less so; this seems to be true with the black oxide of mercury, in which the oxygen is less condensed than in the red oxide: it may be conjectured that the oxide of antimony in which Thenard found only 0.02 of oxygen is in the same state; but in the other oxides no sensible difference is observed, which must be the case, since the heat is able to drive off part of the oxygen, and thus removes the differences of condensation which depend on its proportions: I have compared the reduction of oxide of tin, strongly oxidated by the action of nitric acid, with that of tin in the first stage of oxidation, and have not found any difference in the degree of heat required for the two reductions.

Thenard says, indeed, that the oxide of antimony, precipitated by the acids from the alkaline solution of antimony oxidated by nitre, requires a much stronger fire for its reduction than the others; but it may be conjectured that it owes this difference to a small portion of alkali which it must have retained; for I have shown\* that antimony oxidated by nitre, is a combination of the oxide with pot-ash, and Thenard has determined the proportions of this combination.

378. For a similar reason, oxidation will pass through its different degrees much more easily

\* Mém. de l' Acad. des Sciences. 1788.

when the force of cohesion is destroyed; and this is observed in the metals which have acquired liquidity, by their combination with mercury, and especially in that which they form with the acids: if they are at the lowest degree of oxidation in their solutions, they can, by exposure to the air, pass insensibly to a much more elevated degree; but this observation is only applicable to the metals which exercise an energetic action on oxygen; in the others, the effect may be restrained by the resulting affinity of the acid.

In a similar manner, the oxides precipitated from metallic solutions in which they were but weakly oxidated, in the state of incoherence in which they are, and notwithstanding the saturation they have already acquired, absorb successive quantities of oxygen, and attain a degree of oxidation greater than that which could have been given by heat alone, passing through different shades of colour: but it is to be observed that the colours of the metallic precipitates do not depend on the degree of oxidation alone.

379. Oxygen retains a greater or less quantity of caloric in its combination with the metals as well as in those which it forms with other substances: on this depends a part of the properties which distinguish the oxides in their relations with combustible substances: those of gold, silver, and mercury, retain a great deal, whence it arises that their combination with ammonia detonates, either by a slight elevation of temperature, or  
even

even by compression (*Notes XX. and XXI.*); the oxide of copper, which can also decompose ammonia by an elevation of temperature, does not, however, produce detonation, which shows that the oxygen has much less caloric in it: the oxide of silver yields a more violent detonation than that of gold, or of mercury, so that the oxygen seems to retain more caloric in the first than in the two latter.

380. The affinity of the metals for oxygen cannot be reduced to an exact scale, because the degrees of saturation to which their properties and those of the oxygen arrive, cannot be compared, and because the limits of oxidation do not depend solely on the affinity of the metals for oxygen, but also on their force of cohesion, and even on that of the oxides which they form. Nevertheless, the metals may be distinguished into those which can abandon the oxygen by the action of heat alone; those from which hydrogen can take it; those which require more efficacious means for its disengagement; and, finally, those which experience only an imperfect or doubtful reduction: the metals of the first species are gold, silver, platina, and mercury: it seems that lead has the same property, for when an oxide of lead is exposed to a strong fire in a crucible, globules sublime in the metallic state, and if the remainder does not do the same, it is probably only on account of the great action which this oxide exercises on the earth of the crucible; so that it vitrifies with this earth,



earth, and by that means is preserved in the state of oxide.

Copper is in the second class; for its oxide is reduced to metal by the action of the hydrogen of ammonia, or when hydrogen gas is passed over it at a high temperature. After what I have said above, it will not be surprising that the oxide of lead can be reduced by hydrogen gas at an elevated temperature, as has been shown by Priestley, and more particularly by Guyton, who proved that a quantity of water is thus formed corresponding with that of the oxygen separated from the metal, and that of the hydrogen which is absorbed. Arsenic acid also abandons oxygen to hydrogen, and by so doing resumes the metallic state, according to the observation of Pelletier. Bismuth is probably in the same situation.

The oxides which cannot be entirely reduced by hydrogen, must all have the property of decomposing water; when the hydrogen has produced all its reducing effect on the oxides at the same temperature, their remaining action on the uncombined oxygen will be an equal force: but the quantities of oxygen which each metal can retain in this state are different.

Some metals can be easily reduced by means of charcoal, and others resist it so much that only doubtful reductions can be obtained: nevertheless, a judgment cannot be formed of the affinity of a metal for oxygen by the difficulty of its reduction alone: the fusibility of the metal, the condensation

tion of the oxide have an influence on its reduction, so that when a metal is of very difficult fusion, its reduction becomes so.

Those metals which have a stronger affinity for oxygen can take it from those which have a weaker; thus iron can reduce the oxide of mercury, and tin produces the same effect on the oxide of copper, a property on which is founded the refining of bronze, which is obtained by introducing into a metallic bath the oxide of copper, which yields its oxygen to the tin; but the action of the oxides with each other, and of the metals, permits this disoxidation only to take place in a small number of instances.

The reduction of the metals by charcoal offers different phenomena, according to the force with which the oxygen is retained by the metal; the more strongly the oxygen is combined, the more elevated will be the temperature necessary to weaken this union; so that it is only at the highest temperature that that of platina can be obtained, and that of tungsten and molybdena can scarcely be effected. The effects are also various with respect to the gas which is disengaged, according to the temperature, and according to the fixity of the oxygen: if the metal abandons it easily, the charcoal on its part gives a proportion of carbon and of hydrogen which can immediately form carbonic acid, and water which enters into solution in this acid; but if the temperature is very elevated, on the one side the charcoal tends to give more hydrogen,

gen, and, on the other, the metal yields too little oxygen to complete the two combinations which should be formed (287): then the ternary combination is produced which I have called oxi-carburated hydrogen; hence it arises that, according to the opinion of Cruikshank, the more heat the metals require for their reduction, the more of this gas is produced; but those which are very reducible yield the first portions of their oxygen with more facility than the last; so that in the reduction of these metals by charcoal, as Priestley and Woodhouse have remarked, much carbonic acid is obtained, at the commencement, and little oxi-carburated gas; the proportion of the latter augments as it advances, and towards the end it is obtained nearly alone.

381. The oxides have more or less the property of combining with the alkalis; it seems in general to increase in proportion as the oxidation is more advanced, so that the action of the alkalis can prevent the disengagement of oxygen which would have been produced by heat (375); and it manifestly favours the progress of oxidation in some metals, particularly tin.

If some oxides, such as the oxide of iron, seem to refuse this combination, we are warranted in conjecturing that this difference only depends on the force of cohesion belonging to the oxide: for when the iron is very much oxidized it enters more readily into vitrification with the alkaline earths than when it is but little so.

Such

Such of the oxides as, by their natural dispositions, can receive a great proportion of oxygen, pass at length to a state decidedly acid, and form particular acids.

Arsenic possesses this property in the highest degree: 100 parts of the metal combine at first, according to the valuation of Proust\*, with 33 parts of oxygen. In this state it has properties analogous to those of the very oxidized metals: it dissolves readily in the alkalis, and very little in the acids; it has acquired a fixity greater than that which is natural to it; but it is at the extremity of the proportion of oxygen which it can receive by the aid of heat; nevertheless, it can take a greater proportion when it is treated with substances which contain condensed oxygen, and which retain it feebly: it acquires much more fixity by becoming acid with this new portion of oxygen, so that the proportions of which it is composed produce a greater mutual condensation than in the oxide. If the effect of this condensation is destroyed by heat, the portion of oxygen, which rendered it fixed, disengages in gas, it passes again to the state of oxide, and the volatility which it acquires causes it to escape from the action of heat which tends to disengage the remainder of its oxygen.

This fixed acid passes readily to the solid state, and without doubt could be made to crystallize:

\* Journ. de Phys. Tom. LI.

from this disposition to solidity it possesses the property of forming acidulous salts with the alkaline bases which have less, as is seen in the salt, whose discovery is owing to Macquer, and of producing insoluble salts with the earthy alkaline bases (199).

In passing to the state of acid, the oxide of arsenic acquires 20 ponderable parts of oxygen, which are added to the 33 it had before; so that 100 parts of metal produce 153 of acid. This is nearly the quantity of oxygen taken by iron when it passes to the state of the greatest oxidation; but the same quantity of oxygen produces a different effect with these two metals, which depends on the affinity each has for the oxygen. Highly oxidized iron has not any sensibly acid properties, and arsenic acid has very powerful ones: the iron, by the stronger action which it exercises, saturates the properties of the oxygen with which it can combine, and, for the most part, renders them latent. Arsenic produces the same effect on the 33 parts with which it combines at first; but it preserves much of their natural properties in the 20 parts which are added.

The oxide of arsenic may be compared to oxygenated sulphur and phosphorus, and still more to nitrous gas, which, having no acid property, acquires acidity from the oxygen which combines with it.

Fourcroy has designated the oxide of arsenic by the denomination of arsenious acid, comparing it



it with the sulphureous and phosphoreous acids, in their relation to the sulphuric and phosphoric acids; but the oxide of arsenic does not exercise an action on the alkalis stronger than the other oxides, and several of them have even the superiority over it. It is true, that the acids combine feebly with it; but, in this respect, it is in the same situation as the highly oxidized metals, and the muriatic acid also acts on it more than the others; it therefore seems to me to retain more analogy with the other oxides than with the sulphureous and phosphoreous acids, and that its properties are much better indicated by classing it with the oxides than with the acids, not to speak of the inconvenience of making useless innovations in a nomenclature to which Fourcroy was so useful a contributor. However, its analogy with sulphureous acid may be maintained when it combines with the alkalis, because it then performs the functions of an acid.

Tungstic acid has an indistinct acidity, and seems to differ but little from the oxides, properly so called, which can abandon a part of their oxygen.

Molybdic acid has a more marked acidity, but it only retains that part of the oxygen to which it owes its acid properties, feebly; so that it readily resumes the state of oxide by the action of inflammable substances, and it then passes from a white to a blue colour.

Chromic

Chromic acid, for whose important discovery we are indebted to Vauquelin, seems also to have properties decidedly acid, as far as can be concluded from the experiments which could be made on the small quantities of it yet obtained.

Chromic acid is remarkable for the red colour which it has in that state, and which it communicates to the red lead of Siberia, and to the spinelle ruby : in the state of oxide it has other colours which seem to vary according to the state of the oxidation ; it is thus that it gives a green colour to the emerald.

382. It appears to me to result from the preceding observations ; 1st. That the metals, as well as all the other substances which form combinations, take a proportion of oxygen, which does not correspond with their affinity alone, but with all the conditions which are favourable or contrary to their action on oxygen.

2d. That of these conditions, the temperature is that which has the most influence on the different degrees of oxidation of the same metal ; but that there is a certain term of the temperature which is the most suitable, by the effect which it produces on the force of cohesion of the metal, without too much increasing the elasticity of the oxygen ; so that a lower degree would allow the resistance of the cohesion to predominate too much, and a more elevated degree would give too much energy to the elasticity, and disengage a part of the oxygen which could have combined at an inferior temperature.

3d. That

3d. That the volatility of a metal which oxidates gives it a fixed degree of oxidation.

4th. That in such of its effects as are favourable to oxidation, heat only acts as a force opposed to the cohesion, since, when this obstacle is removed by other means, the oxidation takes place without an elevation of temperature.

5th. That when, on account of its intensity, heat ceases to produce oxidation, other degrees of it may be obtained by means of condensed oxygen, and of circumstances which favour its combination.

6th. That in their reciprocal action with other bodies, the oxides show all the effects of a resulting affinity.

7th. That the properties of oxygen are found to be greater in these effects, the farther the oxidation has advanced; and that, at length, when the qualities of the oxide admit of its combination with a proportion of oxygen, superior to that which gives it the properties common to oxides, it acquires those which characterize the acids.

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### CHAP. III.

#### *Of Metallic Solutions and Precipitates.*

383. THE metals only dissolve in the acids when they are in the state of oxide, as was discovered

covered by Lavoisier : these solutions give rise to a great number of combinations, according to the circumstances in which they are formed ; according to the proportions which enter into their composition ; and according to the degree of oxidation : the insoluble salts and the precipitates which are produced from these solutions likewise offer many varieties : the oxides have also the property of forming combinations with the alkaline bases, of producing triple combinations with these bases, and with these acids, and also of combining together : I shall confine myself here to pointing out the relations which are to be found between the metallic and other substances in their mutual action with the acids and the alkalis, and the general causes of the various properties which are offered by metallic solutions and precipitates : I shall only dwell upon some subjects on which chemists are not yet agreed, the discussion of which I had begun in the preceding chapter.

A metal oxidates in combining with an acid, either by means of the oxygen which it abstracts from the atmosphere, or by the decomposition of the water, or by taking the oxygen condensed in a part of the acid itself.

These three modes of oxidation belong to the metals which have a strong affinity for oxygen ; but the first is the only one which can produce the oxidation of a metal which has but a weak action on oxygen, when it is present with an acid, whose action has, at the same time, but little

energy: thus copper or lead placed in acetic acid, without the contact of the air, do not form any solution; but if the mixture is exposed to the air oxygen is absorbed, and the solution takes place.

If the action of the acid is more powerful, and if it is promoted by the action of heat, the same metal which could only be dissolved by the accession of the oxygen of the atmosphere, acquires, by the concurrence of the more energetic acid, the property of decomposing water, although it did not possess it in itself, and its oxide could be reduced by hydrogen gas: this is observed in copper, which can dissolve in muriatic acid, and yields hydrogen gas; arsenic, which cannot decompose water alone, offers the same property.

The metals whose action on oxygen is very weak, cannot be oxidated in this manner: it is necessary that they should meet with the oxygen in an acid which can yield it more readily than the water; one part of the sulphuric acid then passes to the state of sulphureous acid, while another part dissolves the oxide which forms, without experiencing decomposition: a part of the nitric acid is, in the same way, reduced into nitrous gas, or gaseous oxide of azote, according to the energy of the affinity of the metal for oxygen: finally, in the solutions of gold and platina, which can only take place with nitro-muriatic acid, because they have too weak an action, either on the oxygen, or on the acids, the property possessed by the nitric acid of yielding condensed oxygen readily,



readily, is united to the action of the muriatic acid, which is much stronger than that of the first.

In these solutions, the effects do not depend wholly on the affinity, either for the oxygen, or for the metal, but also on the force of cohesion which forms a resistance.

384. An oxidized metal which dissolves in an acid causes its properties to disappear exactly like an alkali, and saturates corresponding quantities of the different acids, as I have observed with the alkaline bases.

Since my Researches on Affinity, I have investigated this property, by mixing together different metallic solutions which were in a neutral state or nearly so, choosing those in which the mixture would produce a combination which precipitated, or in which the two metals would be precipitated, and by making similar mixtures of metallic solutions with solutions of neutral salts which would produce a precipitate by means of their acid: in these experiments, I found only the nitrate of silver and the oxygenated muriate of mercury whose mixture produced a change in the state of the neutrality; the liquid part became acid.

The principle which I have just laid down may be considered as general, with a very small number of exceptions, and on this ground, the capacity for saturation of the metallic substances may be compared with that of the alkaline bases (47);

thus, according to the valuation of Proust, 100 parts of oxide of silver take nearly 29 of muriatic acid to form muriate of silver ; but 100 parts of ammonia saturate 200 parts of the same acid : the capacities for saturation of these two bases will therefore be in the relation of 29 to 200 : the muriate of silver must be considered as being in the same state as the muriate of ammonia, when the latter is exactly neuter ; for if, for example, it is formed by mixing nitrate of silver, which is neuter with muriate of soda, the super-natant liquid shows that the neutral state has not been changed by the exchange of base ; but the capacity for saturation varies according to the state of oxidation, and in this comparison it is necessary to employ solutions which can produce a neutral state, or nearly so.

All the metals cannot produce a neutral solution, but some necessarily require an excess of acid, without which their oxide separates, forming an insoluble salt, and it only retains with it a greater or less portion of acid, according to the effect of its force of cohesion at a certain degree of oxidation, and that of the action of the water on the acid, which varies according to its quantity, according to the temperature, and according to the energy of the acid.

385. Before Rouelle, the ideas on the character of the salts and on their differences were only confused : that celebrated chemist threw much light on this subject, which embraces a great part

part of chemistry, and which is interesting in all its considerations: he distinguished the salts which could separate into soluble salts, having an excess of acid, and into insoluble salts with the least acid possible, which he considered as neutral; he, however, made another class of salts perfectly neuter, and of a mean solubility\*.

He also showed that the precipitates obtained by means of the alkalis, contained a portion of acid, by which they were analogous to the salts with the least acid; but that they also retained a part of the substance which was employed to precipitate them; this, however, does not always take place.

Finally, he distinguished from the preceding precipitates, those obtained from a metallic solution by means of an acid, and he showed that these precipitates were salts with the least acid.

There is not, perhaps, any inquiry that has thrown so much light on a multitude of combinations which the want of method had permitted to be confounded, and which has pointed out the relations between all those which chemistry might produce with more accuracy; nevertheless, many chemists have neglected the observations of Rouelle, particularly in classing the elective affinities; others, on the contrary, have considered them as too precise.

386. At the term at which Rouelle stopped, it remained to inquire, if the proportions which form-

\* Mém. de l'Acad. 1754.

ed the salts with excess of acid were constant, so that there could only be two combinations, those with excess of acid, and those with the least acid; if combinations could not exist in intermediate proportions; and if these proportions depended on circumstances which could modify the reciprocal action of the metallic oxide and the acid, but which were only to be considered as an obstacle that might be removed in other circumstances: it must be remarked that Rouelle had the circumspection not to assign causes to the separations which he observed, and which, at that time, were enveloped in such obscurity as required ulterior labours to dissipate.

Several chemists, therefore, consider it as a principle which needs no farther examination, that combinations are formed in determinate proportions, and if proportions remote from them are discovered, which necessarily happens in many cases, they are supposed to be only a mixture of combinations, of which one has the limited excess, and the other has the smallest possible quantity of acid; if a super-abundance of acid is found, it is not in combination.

I have combated this opinion in my *Researches into the Laws of Affinity*, and have endeavoured to show that an acid may be combined with an oxide in different proportions, which are established according to the circumstances which may augment or moderate the reciprocal action of the two substances, and according to the properties of the combinations which form: I have applied my observations both to the combination  
of



of the oxides with the acids, and to the oxidation of the metals : the state of these two species of combinations depends on the same causes.

387. If we return to the observations of Rouelle, from which the opinion I discuss is derived, we shall see that when mercury and sulphuric acid are distilled, by a sufficient fire, a white and dry mass remains which has supported a fire superior to that which could produce the distillation of the free acid, and which deliquesces in a moist situation, and becomes liquid and transparent, without any separation ; if, on the contrary, a quantity of warm water is added to the white mass, or to the transparent liquid obtained from it, a yellow deposit is formed which is the salt with the least acid ; by evaporating the liquid after this separation, it yields crystals which are the salt with excess of acid.

We have here three combinations, that which becomes liquid by deliquescence, and which contains all the mercury and all the acid ; that which crystallizes with an excess of acid ; and, that which has the least acid : if the latter is washed, a salt continues to separate from it, which, relatively has more acid ; so that what remains contains more and more of an excess of oxide ; whence it also results that in the first separation, the precipitate retains so much less of the acid as the quantity of water brought into action has been greater, until the insoluble salt attains a point at which it completely resists the action of the water.

But,



But, it will be said, the liquid formed by the deliquescence contains the two salts, and their reciprocal action renders that soluble which is not so naturally : it must then be admitted that the salt with the least acid, which separates at first, is also a compound of the two salts, and that it is only at an indeterminate term that it can be finally freed from that which has an excess of acid.

It will therefore be supposed that the soluble salt, and that which is insoluble, exercise such a reciprocal action that the first can entirely overcome the insolubility of the latter : but is not a force capable of this effect, perfectly equal to that which produced the combinations? What is the ideal distinction attempted to be established, in not concluding from observation that the sulphuric acid divides its action between the oxide and the water ; that these substances act in the ratio of their quantity, so that when the water predominates, it separates a portion of the sulphuric acid, which then only retains a certain quantity of the oxide, the remainder of which is insoluble, and retains another part of the acid ; and, that these divisions are made according to the state of the opposite forces? We may observe that, in the contrary opinion, it is requisite to admit the chemical action of water, by making a distinction between the affinity which it exercises, and that of the two elements of the combination.

The only difference I perceive between the action of an alkali which produces the metallic precipitates,

precipitates, and the action of the water, is that arising from the energy, which is greater in the alkali, and leaves less acid in the precipitate, laying aside the very variable quantity of the precipitant which may enter into the composition of the precipitate, in proportion to the affinity which it has, either for the acid or for the oxide. The alkalis also differ from each other according to the force of their alkalinity, their concentration, and the other circumstances which accompany their action.

The same observations are applicable to the properties which Rouelle found in the nitrate of bismuth and the oxygenated muriate of antimony. I might here accumulate facts which prove that, both in these products of chemistry, and in natural combinations, a great variety of intermediate proportions between the salts with excess of acid and the salts with excess of oxide, are met with : I shall confine myself to referring to those which are set forth in the memoir which I subjoin (*Note XXII*), and which was presented to the Institute by A. B. Berthollet, my son. I shall only add one example taken from the analysis of the arseniates of copper : Chenevix, to whom we are indebted for this analysis, describes six species, in which the proportions of oxide and acid are different : he formed an artificial arseniate in which the acid was in a smaller quantity than in any of these species ; is it not probable that none of these species have constant proportions, and that those which are intermediate may exist ?

We

We have, however, observed that several combinations are formed in certain proportions by the degree of condensation which the elements experience in those proportions; that this cause may also limit the combination of the two elements to one or two determinate proportions as we have observed on the oxidation of mercury (371).

388. It is the same with the state of oxidation of the metals, and with their proportions in the combinations which they form with the acids: an acid can generally combine with a metal within a certain latitude of oxidation; but the saturation is varied by the different degrees of oxidation, the quantity being the same, or the proportion of the acid will be different; the cohesion belonging to combinations sometimes determines a separation into two combinations, one of which is soluble, and the other insoluble; the relation of these two combinations varies according to the circumstances, as we have seen in the sulphate of mercury; but it may have fixed proportions, particularly when the action of the acid is energetic, like that of the muriatic acid; so that combinations may exist which are constant both in the proportion of the acid, and in the degree of oxidation, and there is nothing particular in this species of combination.

Such is the case with muriate of mercury, not only with respect to the oxidation, but also to the proportions of acid with which it can separate: it appears to me that, in forming a combination

nation with the muriatic acid alone, which separates by its insolubility, or crystallizes, it can only be obtained in two states; either in that of oxygenated muriate of mercury, or in that of muriate of mercury, or mild mercury: I have given a contrary opinion in my Researches into Affinity, but in subsequent experiments, with the exception of one, of which I shall speak hereafter, I have not found any sensible difference, in respect of the oxidation and the other properties, between the preparations which the insoluble muriate yields by different sublimations: even that which the precipitates of mercury allow to sublime by the process of Bayen, did not seem to me to differ from the common sweet mercury; but these precipitates give more or less saline sublimate according to the circumstances of the precipitation, and if an excess of alkali is employed, scarcely any is obtained; so that the proportion of the acid eliminated by the alkali, and of that which is retained by the oxide, may vary greatly.

This division into two oxides, of which each has a determinate degree of oxidation, observed in the muriates of mercury, as well as that of two fixed proportions of acid and oxide which takes place in some metallic combinations, cannot be considered as the most general fact; the following observations seem to prove this, although there are some circumstances in which it is difficult to determine whether only one degree of oxidation is

is established, or two distinct states exist at the same time.

389. The oxides readily yield a portion of their oxygen, or even all of it to the same metal which has not a sufficient quantity of it to dissolve in an acid, and thus an oxide may be partly reduced that another portion may be more oxidized.

Chenevix having put oxide of copper, which had only  $11\frac{1}{4}$  of oxygen, into phosphoric acid, it effected the solution: but for this one part of the copper gave all its oxygen to that which entered into solution, and resumed the metallic state.

Proust relates that mercury, left in a solution of oxygenated muriate of mercury, changes into mild muriate; and Fourcroy has made a similar observation on the highly oxidized sulphate of mercury.

The greater affinity of a metal which is but little oxidized in a combination, for oxygen, gives it the property of taking it from another metal which is also in solution, and in a more advanced stage of oxidation: it is thus that muriate of tin, but little oxidized, abstracts the oxygen from sulphate of copper, and reduces it to a weak oxidation, as is shown by the elegant experiments of Proust on this subject.

In this change of oxidation, does the tin pass, at once, from the least to the most oxidized state? If its solution is left exposed to the air, it gradually attracts the oxygen, as has been shown by

Pelletier:



Pelletier: it is the same with muriate of copper, and, generally, with all the metals which have an energetic tendency to combine with oxygen: when they are in solution, and but little oxidized, they oxidate more and more until they pass to the most oxidized state to which the solution can attain; then it commonly happens that a part becomes insoluble and separates, retaining a certain quantity of the acid. Is there not a great probability that the oxidation then advances by progressive steps, and that there is no other exception but in those rare cases in which the combination, passing at once to the insoluble state, retains very little action on the oxygen, as we have seen in the muriates of mercury?

Proust has shown that when iron is put into a solution of the very oxidized sulphate, which always has a great excess of acid, the sulphate passes to the least oxidized state: the iron is therefore capable of taking a part of the oxygen from that which is much oxidized, to dissolve into a uniform state with it; this fact, however, does not give a simple result: during this action hydrogen gas is disengaged, and a yellow precipitate is formed, arising from the very oxidized iron which retains a portion of acid: but in this precipitate, whose oxide is already red, as is proved by the action of the alkalis, the iron is in a lower degree of oxidation than that of a sulphate which has been well calcined; for water can separate all the acid from this, which it cannot do with the first.

I mixed

I mixed a solution of the least oxidized sulphate of iron with a solution of the most oxidized, the mixture remained several days, at the temperature of winter, unchanged; but in summer, a similar mixture became turbid in about 24 hours, and a yellow precipitation took place: if it is exposed to heat, it becomes turbid as soon as it begins to be warm, and a deposit is formed: a division of the oxygen is therefore made, at least at a certain temperature, and the acid can no longer hold all the metal in solution which has taken a mean oxidation.

If the liquid is evaporated without communication with the air, as soon as the precipitation of which I have spoken is made, crystals of a sulphate but little oxidized are formed, and a much more oxidized sulphate remains in solution, so that a new division of the oxygen is made when a crystallization can be established.

Even when a separation is made, the salt which crystallizes may not be constant in its composition: in the fabrication of sulphate of iron, and especially when the iron is dissolved immediately in the sulphuric acid, the first crystals which are obtained are nearly without colour, those which succeed in the subsequent crystallizations take more and more colour, to a deep green, and, at the end, there is an incrySTALLIZABLE liquid which is in the state of red sulphate.

Thus it is evident that a division of the oxygen is made during the course of the crystallization, and

and that the sulphate of iron which crystallizes has not fixed proportions of oxygen, like the mercurial salts ; it may be more or less oxidized, and it passes by insensible gradations from one state to the other.

This variation, not only in the proportions of the acid and the oxide, but also in the degree of oxidation, is particularly observed in the precipitates which are obtained, as will be seen from the examples given in the note.

Mercury itself only appears to take two constant states of composition at the moment when it can separate into two combinations: when this metal is dissolved in nitric acid, with the aid of heat, much nitrous gas is disengaged, and the most oxidized nitrate is formed ; but when this is produced, it dissolves a fresh quantity of mercury, without any disengagement of nitrous gas, as had been observed by Bergman. The mercury which was first dissolved, therefore, yields oxygen to that which enters into solution without the disengagement of nitrous gas : from the preceding observations it is not probable that it makes an uninterrupted transition from the most oxidized nitrate to the least ; but the combination must be progressive, and the two extreme combinations, occasioned by the mixture of the muriatic acid, can only be formed at the moment when the separation of the soluble, or the insoluble salt from the water is determined by the action of this acid.

390. The following observation shows with what facility this transfer of oxygen takes place : if nitrate of mercury, of a mean oxidation and which has not an excess of acid, is mixed with muriate of soda, an abundant precipitate of a muriate, but little oxidized, is obtained ; but if the solution of mercury has an excess of acid, there is only a very small precipitation and the mercury is nearly all reduced to oxygenated muriate ; nitrous gas is disengaged at the same time, so that the mercury only takes the oxygen which it required to form the soluble combination, at the moment when the action of the muriatic acid determines this oxidation : this easy change of state shows the necessity of circumspection in drawing conclusions from the metallic combinations formed by means of a substance which separates them by precipitation.

In the above instance, the nitric acid contributes, by its excess, to the production of the oxygenated muriate, instead of the insoluble muriate which would otherwise have been formed, on the one hand, because, it can yield oxygen to it, and on the other, because it makes a division of the oxide, as is very evident when this acid acts on sweet mercury which is already formed.

If, therefore, sweet mercury is treated with nitric acid, it dissolves it, yielding much nitrous gas ; crystals of oxygenated muriate of mercury are obtained by evaporation, and the residue is nitrate  
of

of mercury, which gives the red oxide by evaporation and desiccation : one part of the nitric acid has therefore taken its share of the mercury, while the other gave up its oxygen\*.

The foregoing considerations seem to me to prove that the combinations of the oxides with the acids have no property which distinguishes them from those of the alkaline substances, except the variable force of the combination which depends on the degree of oxidation ; that, besides, there are terms of saturation in these combinations at which they are separated by the force of cohesion peculiar to the proportions, compared with the action which the acid is able to exercise ; but, that almost in all cases this obstacle only requires a greater or less addition of force in the acid, that the separated salt may be redissolved, and receive very different proportions, in the liquid state, in which the elements act in the ratio of their affinity and of their quantity (210).

Since the affinity of the oxides for the acids is in general very inferior to that of the alkaline bases, water can produce separations in them with more facility, by the action which it exercises on the acid ; it then occasions a separation into a liquid combination and an insoluble combination ; the proportions of each depend on the forces which are in opposition.

The alkalis produce a similar separation, but with more energy ; the precipitates, therefore,

\* Mém. de l'Acad. 1780.



generally retain a portion of the acid, but this is varied by the energy of the alkali and by the affinity of the oxide for the acid.

391. With respect to the oxidation, these metallic solutions show little difference from the other means by which it can be effected, and which have been examined in the preceding chapter: it appears that in general the metals can dissolve from one term of oxidation to that in which it ceases to be possible; but there are some metals which, by their combination, pass from one extreme of oxidation to another, as we have observed in the simple oxidation; in some circumstances it is difficult to determine whether the oxide takes a uniform state of oxidation, or the oxygen is unequally divided between the different parts.

If a metal has a strong affinity for oxygen, this affinity continues to have its effect when the metal is in solution, or even when the combination is crystallized, so that the state of the oxide, and consequently that of the combination, experiences a change which has only the greatest oxidation for its limit.

On the contrary, the metals which have only a weak affinity for the oxygen, form solutions and salts which do not change their state in the air, such are the solutions and the salts of mercury, silver, and gold. The acids seem in general to have much more action on the  
metals

metals which are little oxidized than on those which are much so, when these metals are capable of passing readily to different degrees of oxidation: for example, iron requires a greater or less excess of acid, when it is very much oxidized, to retain the oxide in solution; consequently, if a solution of sulphate of iron is left in the air, the metal, notwithstanding the action of the acid which tends to maintain it in the state in which it exercises the most powerful action on it, continues to oxidize; but the power of the acid diminishing in the same proportion, a portion of the oxide, by forming a very oxidized combination with the smallest quantity of acid, precipitates; what remains in solution is retained by the overplus of the acid, so that the combination is continually removing farther from the neutral state: at length the action of the oxygen on the metal is balanced by that of the acid, and the liquid attains a state of equilibrium.

The oxides, therefore, become so much the more insoluble as their oxidation has made greater progress; hence it arises that they do not dissolve when they have attained a high degree of oxidation, and as nitric acid can readily occasion this strong oxidation, some metals will not remain in solution with it, unless its action is much weakened.

392. For this reason, the muriatic acid, which exercises a more powerful action than the other acids, retains the highly oxidized metals more strongly, and dissolves the oxides when their power has ceased:

there is another circumstance also which favours this solution; since it has itself the property of combining with oxygen, its action is divided when it meets with a metal which is too much oxidized; one part takes the excess of oxygen, and forms oxygenated muriatic acid, another effects the solution of the metal, reduced to a lower oxidation: the formation of oxygenated muriatic acid by oxide of manganese is founded on this double action; but if oxygenated muriatic acid is poured into a solution of muriate of manganese, the oxide resumes the oxygen and precipitates, so that its separation can only be effected by means of heat.

The oxygenated muriatic acid generally yields its oxygen to the metals in this manner, so that the oxides afterwards act on the muriatic acid by a resulting affinity, and the alkali which separates them retains only simple muriatic acid (319); nevertheless, it can produce a super-oxygenated combination when a very oxidized metal is presented to it: we are indebted to Chenevix for a new investigation of these combinations, which he formed principally with the oxide of mercury and that of silver: in the formation of these salts, which, as he observes, deserve the name of super-oxygenated, or hyper-oxygenated, it appears that the oxygenated muriatic acid divides into two parts, one of which is reduced to the state of muriatic acid, and the other is surcharged with oxygen, as takes place with the alkaline bases\*.

\* Philos. Trans. 1802. Journ. de Phys. Tom. LV.

The sulphureous acid acts variously on the metals ; some decompose part of it to dissolve in the other part ; iron and tin are of this description : a portion of sulphur combines with a certain quantity of metal, but another part remains in solution, and forms a sulphurated sulphite: the oxides act differently ; for example, oxide of manganese quits the superfluous part of its oxygen, and passes with the acid to the state of sulphate: there are also some which can be reduced to the metallic state by yielding all the oxygen ; this takes place with gold when a solution of it is mixed with sulphite of soda\*. Thus a great variety of results may be obtained according to the metals, according to their affinity for oxygen, according to the state of their oxidation, and according to the circumstances which can change the reciprocal action of the metal and of the oxygen combined with the metal, and of that which is combined with the sulphur.

393. I had conjectured (*Recherches sur les lois de l’Affinité*) that the affinity of the muriatic acid did not experience a diminution of action by the progress of the oxidation ; but it appears to me that the difference observed in this respect depends only on the stronger affinity which the muriatic acid exercises with respect to that of the sulphuric acid and the nitric acid: I rely on the following experiments.

\* Ann. de Chim. Tom. II. Fourcroy and Vauquelin. Journ. de l’Ecole Polytech. Cahier VI. Ann. de Chim. Tom. XXIV.

Proust has observed, that mercury, kept in a solution of oxygenated muriate, is changed into sweet mercury ; he also remarks, that this metal forms sweet mercury when it is kept in the red muriate of iron, while it remains unchanged in the green muriate : Boullai exposed a solution of oxygenated muriate of mercury to the light, oxygen gas was disengaged, a certain quantity of mild muriate precipitated, and the liquid reddened the tincture of turnsole\* ; so that the action of light is sufficient to decompose the oxygenated muriate of mercury, but when it is brought to the state of sweet mercury, it ceases to act on it. It is to be observed, that in this experiment, light disengaged oxygen gas and muriatic acid, while it only separated muriatic acid from muriate of silver (128).

Gay Lussac mixed corrosive mercurial muriate with red oxide of mercury in a retort ; at first the former sublimed without experiencing any alteration ; afterwards, the heat having been increased, the oxide was reduced, and sweet mercury formed by volatilizing : having distilled some precipitate of corrosive mercurial muriate by a regulated fire, at first a corrosive mercurial muriate sublimed ; but by the augmentation of the heat, the oxide was reduced, and changed the sublimate into sweet mercury.

Adet has shown that the oxygenated muriate of tin can dissolve more of the metal, without a disen-

\* Ann. de Chim . Tom. XLIV.



gagement of hydrogen gas, and that it then forms a combination analogous to sweet mercury: the muriatic acid, therefore, must also have a stronger tendency to combine with tin which is but little oxidized than with that which is greatly so: it must experience a greater saturation of its properties, and be more strongly retained by it\*.

The same chemist has made an observation which deserves to be noticed: the fuming muriate of tin takes the solid state, by combining with water in the proportion of 22 to 7; this effect is accompanied with a disengagement of heat: in this case, therefore, the water exercises a powerful action, and by it augments the reciprocal affinity of the integrant parts of the combination: it is the principle of the solidity which they acquire, while in the generality of other circumstances it produces a solution, or the separation of a liquid and a solid combination.

394. The metallic precipitates owe their differences to the greater or less quantity of the acid which they, perhaps always, retain, when an excess of alkali is not employed, according to their degree of oxidation, which varies their affinity for the acid according to the concentration of the alkali made use of, according to the species of the alkali, and, finally, according to all the circumstances capable of changing the state of the forces which are in action: they sometimes retain a portion of the

\* Ann. de Chim. Tom. I.

alkali; according to Proust, the precipitate of oxygenated muriate of mercury by lime, contains 0.01 of its weight of lime; those produced by pot-ash and soda did not give me any traces of them, but ammonia enters into the precipitate which it forms in a considerable quantity, as was observed by Bayen, and this precipitate contains a sufficiency of acid to be, in great part, reduced into sweet mercury, by sublimation: if by mixing oxygenated muriate of mercury and muriate of ammonia, the salt which is known by the name of *alembroth*, is formed, pot-ash and soda produce in it a white precipitate which sublimes entirely in sweet mercury. In this circumstance, therefore, pot-ash and soda act in the same manner as when they precipitate the solution of phosphate of lime in an acid (66). In respect of the oxidation, these white precipitates must not be blended with the other insoluble muriates: they can dissolve in nitric acid without any disengagement of nitrous gas, so that the mercury is very much oxidized in them; by sublimation they pass to the state of sweet mercury, but it is by the decomposition of the ammonia that this change is effected, and azote gas is disengaged; at the commencement of the operation, a little muriate of ammonia sublimes.

The sweet mercury obtained in this operation is yellowish, particularly that which is the least raised; and it is attacked with difficulty by the nitric acid which yields a great quantity of nitrous gas: it appears

appears to me to give traces of a smaller proportion of oxygen, and perhaps of acid, than is found in the common sweet mercury (388).

The alkalis can carry off the acid which the oxides have retained, provided they do not themselves dissolve them, and they then occasion the disappearance of the colour which the precipitate owes to the acid, and which is capable of causing such a change in that which belongs to them, that the precipitate obtained from the oxygenated muriate of mercury by ammonia, is white, although the oxide which it contains is red: the sublimate obtained from this precipitate is also white, although its oxide is passed to the state of black oxide.

The solution of a metal but little oxidized takes oxygen from another which is in a more advanced degree of oxidation, as is particularly shown by the solution of tin with that of copper and that of mercury (389): a metal also shares the oxygen and the acid with a metallic solution; but it sometimes happens that it is precipitated by another in the metallic state, so that then there is no distribution either of acid or oxygen; but both abandon one metal entirely to combine with the other.

395. Since chemistry has introduced its explanations of the positive action of substances, these latter precipitations have been attributed to the difference of the affinity of the metals for oxygen; but if this cause, which is undoubtedly of great consequence

consequence in the phenomenon, was the only one which acted, a metal could only take a more or less considerable part of the oxygen with which another was combined, and this having arrived at a certain degree of oxidation would separate in this state; besides the effect should correspond exactly with the difference of the affinities, which is not the case: for example, copper, by simple contact precipitates the solutions of mercury; but iron only does so slowly, and it precipitates nearly all the solution of oxygenated muriate of mercury in sweet mercury; nevertheless, iron has a much greater affinity for oxygen than copper; another, and even a determining cause, must therefore contribute to the effect.

Vauquelin has observed\* that the affinity of the acid for each of the oxides must be taken into the explanation of these precipitations; but this cause, as well as the preceding, could only occasion an unequal division.

I have observed in my *Researches into the Laws of Affinity*, that the reciprocal affinity by which two metals tend to combine, or even the reciprocal affinity of the *moleculæ* of the same metal, being of the number of the forces which exist in the phenomenon, it must no more be lost sight of in the explanation to be given of it, than in the other circumstances in which I have shown that it is often the determining cause of the separations which are produced.

\* *Ann. de Chim.* Tom. XXVIII.

In fact, if this force acts between two metals, the combination which it should form will be found, and if this combination is found, the effect of the force which produced it should be acknowledged.

Now when the mercury is precipitated by a plate of copper, the mercury is not deposited at a distance from the copper; it is found to be immediately combined with it.

If lime was put into a solution, and was found to be changed into a sulphate, would it not be said that its affinity determined the combination which was formed?

When silver is precipitated by copper, it is not pure silver which is found in the precipitate, even when it does not adhere to the copper; but the precipitated silver contains a certain proportion of copper, which must have been precipitated from the solution by a reciprocal reduction: it is the same with gold; the precipitate produced by copper in its solution is of a deep reddish colour, which can only be attributed to the copper retained with it: the acetate of copper also produces a precipitate in it of a high colour, and which contains a little copper, according to the testimony of Wasserberg. If copper is rubbed with muriate of silver, it becomes plated, or the silver incorporates with it by the action of the mutual affinity; the processes of gilding and plating consist in thus separating the gold or silver contained in an amalgam or in a solution, by the affinity of a metal which retains it in combination at its surface. Vauquelin having precipitated



precipitated nitrate of zinc by lead, found that 50 parts of the first metal formed a precipitate of 138 parts, which was composed of the two metals\*.

It, therefore, seems to me that in these precipitations it is the affinity of one metal for another which determines its disoxidation; that while one part of the metal combines with that which precipitates, another acts by its affinity on the oxygen, and on the acid, and that this latter effect would be generally limited to a more or less unequal division, either of the oxygen or of the acid, without the concurrence of the reciprocal action of the two metals.

In this example which I have borrowed from Vauquelin, the lead was able to precipitate the zinc, which has nevertheless a much stronger affinity for oxygen: all that can be said on the difference of affinity of the oxides for the acid is vague, until their capacity for saturation has been compared, and this capacity is also varied by the degrees of oxidation.

What I have said on the affinity of two metals is applicable to the reciprocal affinity of the molecule of the same metal; thus when the copper is applied to the surface of the iron, the continuation of its precipitation is determined by the action of the stratum of copper which is formed, as a salt in solution is induced to deposit on a crystal; but the latter effect is very limited, because the action of the water

\* Ann. de Chim. Tom. XXVIII.

acquires power as the salt is deposited, unless evaporation carries off the water which has become superabundant; but in the precipitation of a metal, while it separates, it dissolves the precipitating metal; so that the circumstances favourable to the precipitation do not change.

396. In their action on the acids, which we have examined thus far, the oxides offer properties analogous to those of the alkalis, except that their tendency to combination is varied by the degrees of oxidation; but they have also another distinguishing character, which is, that they can combine with the alkalis, and form combinations with them which are sometimes more energetic than even those with the acids, so that they exercise the functions of both the alkalis and the acids\*. In this they correspond with alumine and silex (349-352), and they are different from the alkalis which show little reciprocal action; we must examine the differences which they offer in this respect, and endeavour to discover the causes of these differences, as far as the state of our knowledge, which is yet but little advanced on this subject, will admit.

Some oxides dissolve in one alkali and not in another: in general, ammonia dissolves the oxides more readily and more abundantly than the other alkalis; thus it dissolves oxide of copper, and forms with it the crystals described by Sage,

\* Mém. de l'Acad. 1788.

and pot-ash does not dissolve this oxide, as has been observed by Vauquelin, or at least it only takes a very small quantity : ammonia readily dissolves the oxides of zinc, cobalt, nickel, and chrome.

There are, however, oxides which are soluble in the fixed alkalis, and not in ammonia, such is the oxide of manganese ; but it is natural to attribute this difference to the force of cohesion, which must be diminished by the action of heat to enable the combination with an alkali to be effected, and the ammonia is volatilized by it ; since when this reason does not exist, it offers the same superiority over the other alkalis as in the action which it exercises on the acids. The decomposition of the ammonia and the disoxidation of the metal, which diminish its action on the alkali, may intervene in this effect, as will be seen.

This property may be employed to form a great number of combinations, hitherto unknown, with the different alkalis, and the oxides which dissolve, with facility : thus the oxide of lead, which is soluble in ammonia and in fixed alkali, can form a combination with lime, and probably also with strontian and barites ; but these latter combinations will generally be insoluble because their two elements have a great disposition to solidity.

The difference of the action of the alkalis on the oxides should be observed with attention, because it is very useful to analysts in the separation of the different oxides ; thus, in the analysis of  
brass,

brass, Vauquelin employed the property of potash, which dissolves the oxide of zinc, but not that of copper, with success.

397. Some oxides, and particularly that of gold, have such an action on ammonia, that when the solution of the latter is precipitated by ammonia it takes a fixed proportion: the combination which is formed even resists the action of sulphuric acid, diluted with a certain quantity of water, and of nitric acid: if muriatic acid is capable of dissolving it, it is only necessary to form a new precipitate with a fixed alkali, and it will still be the combination of the oxide with ammonia: besides, the oxide of gold can abstract a portion of ammonia from the neutral ammoniacal salts, and become detonating\*.

When ammonia is combined with an oxide, it may be decomposed by the combination of its hydrogen with the oxygen of the oxide; hence the detonations when the oxygen has retained a great proportion of caloric: in the liquid state, the cuprate of ammonia is decomposed by the heat alone which is communicated to the liquid. It is not only when the ammonia has been able to form a combination with an oxide, that it can experience a decomposition by the action of this oxide, but it is sometimes destroyed without entering into combination with it, so that, by this mutual action, the oxide is brought to a state of oxidation very

\* *De calce auri fulmin.* § VIII. XII.

remote from the former, whether a metallic solution is precipitated by the ammonia, or this alkali is made to act on a greatly oxidized metal, as was shown by Fourcroy, in some very interesting experiments on the solutions of iron, manganese, and some other metals, as well as on the metals when greatly oxidized\*. This is a reason why ammonia must be unable to dissolve some oxides notwithstanding the alkaline power which it possesses. I have already observed that the oxides have the property of combining with the alkalis in a degree proportionate to their greater state of oxidation; if, therefore, the action of the ammonia begins by de-oxidating the metal, it proportionally diminishes the disposition to combine with it, and renders it incapable of overcoming the force of cohesion.

But the alkaline power of ammonia, compared with that of the other alkalis, is shown in its greater disposition to form triple salts, and it is particularly with the muriatic acid that it forms these salts; because, after the fluoric acid which has been so little examined, it is this which exercises the strongest action of acidity.

After ammonia, magnesia must be the most disposed to form triple salts, since it is next in alkaline power(87).

If ammonia is poured into a solution of silver which is in a neutral state, there is a little precipi-

\* *Mém. de l' Acad.* 1788.



tation ; but there is not any if the acid is in a small excess, because the oxide of silver forms a triple salt with the ammonia and nitric acid, which may be made to crystallize, and which has been noticed by Margraf and by Bergman ; nevertheless, this triple salt abandons part of the oxide of silver, if there is not an excess of acid to saturate the two bases, as Higgins showed long ago was done by the ammonia with the combinations of magnesia (345).

Among the oxides, none shows a greater disposition to form triple salts than the oxide of platina, so that notwithstanding the great excess of acid in its solution, it takes, according to the observation of Bergman, a part of the pot-ash and of the ammonia from the neutral salts with these bases, and forms a slightly soluble triple salt, which precipitates if there is not much liquid ; nevertheless a part of the oxide remains in the solution whatever quantity of alkali may be added to it, and soda, which has not the property of forming a slightly soluble salt with it, does not produce a precipitate, except when it is in a great proportion.

398. This disposition to produce triple salts is a new relation with alumine, and also with silex, which does not wholly separate from neutral salts until its force of cohesion is augmented by desiccation : in these different substances it depends on the disposition which it has to unite either with the acids or with the alkalis.

The oxides exercise a mutual action which is sometimes sufficient to produce a combination which separates from the acids: gold and tin offer an example of this property which has hitherto been little observed. Erxleben has shown that the purple precipitate of Cassius is a combination of the two oxides which has abandoned their acid; his observations prove that the oxidation must only be in a moderate degree for this effect to take place, and that if the solutions are boiled, the oxidation being too far advanced, opposes it\*: in other circumstances this mutual action of the oxides promotes their solution in the acids: thus Tillet was enabled to dissolve platina in nitric acid, by previously alloying it with gold and silver, which by their action procured the solution of the first metal†.

399. The great number of combinations which the oxides can form, and the varieties resulting from the degree of oxidation, call for the assistance of the methodical nomenclature, that language may represent them concisely and without obscurity.

We have seen that the oxides have the property of forming combinations with the alkalis, it was formerly proposed to consider the oxides as acids, because they fulfilled their functions; Chenevix has rejected these convenient denominations in

\* Wasserberg, Instit.

† Mém. de l'Acad. 1779.

the excellent observations which he has made on the nomenclature, because the common termination might occasion an oxide to be confounded with an acid: the nomenclature can only be intelligible to those who have an exact idea of these subjects; when the terms plumbate of pot-ash or lime, argentate of ammonia, are employed, it must be recollected that on these occasions the oxides have a property analogous to that of the acids; but that, beyond this circumstance, they must not be blended with the acids; nevertheless, by means of these denominations, the substances brought into action, the combinations which they form, and those which succeed them, are known without embarrassment: this observation is applicable to many cases in which the direct signification of the terminations employed in the nomenclature may be diverted to indicate the elements which are combined or are present with precision and without confusion: but this licence should be used with circumspection.

The ambiguity resulting from the denomination of oxygenated, which is given to the oxygenated muriate of mercury and to analogous combination, and which seems to indicate that these combinations are owing to the oxygenated muriatic acid, while it is the oxide which really retains the oxygen, may be avoided by employing the term super-oxidated, as was proposed by Boullai.

## CHAP. IV.

*Of the Combination of Metallic Substances with Sulphur, Phosphorus, and Charcoal.*

400. SULPHUR and phosphorus, which possess several properties analogous to those of the metals, and whose affinity for oxygen also constitutes the predominant character, combine with them, and form compounds which may be compared to alloys.

The metallic sulphurets are brittle and friable, and, nearly all, more fusible than the metal which enters into their composition, especially when the metals have but little fusibility alone; so that this result of the properties of the elements is found in this species of combination as well as in the others.

There are only zinc and gold which refuse this combination; but we shall see that this difference depends only on some conditions.

The metals can combine with sulphur in very various proportions, and the combinations which are thus formed have different properties according to their proportions: I am, in this case, again in opposition to the opinion of Proust, who asserts,

serts \*, that *by the invariable law of proportions, sulphur and iron are fixed at  $\frac{6}{100}$* ; but he acknowledges that pyrites may contain a variable surplus, as far as 20 parts and upwards: is not this sulphur which gives peculiar properties to the pyrites; which takes a crystalline form with the rest; which defends the pyrites from spontaneous decomposition; which resists the action of other substances which readily dissolve it; is it not retained by a force of combination? If heat can easily drive off the sulphur, considered as foreign to the combination, this is only a common property of all substances, which resist the expansive action of heat so much the less as they are in greater proportion in a fixed combination; for chemical action is diminished by the progress of the saturation.

Proust affirms the same thing of sulphate of copper, or cupreous pyrites; he considers that part of the sulphur which can be readily driven off by heat as foreign; only invariable proportions remain; but this chemist admits that the black copper is a sulphuret dissolved by copper: this solution, in reality, offers successive proportions of sulphur and copper.

He also pretends †, *that an invariable dose of sulphur, fixed by nature, attaches to antimony, and that the power of augmenting or diminishing it, is not given to men.* He fixes this proportion

\* Journ. de Phys. Tom. LIII.

† Journ. de Phys. Tom. LV.



at 35 parts to 100 of antimony; he, however, found sulphurets of commerce which had an excess of sulphur, and which could still dissolve 7 or 8 parts of antimony in 100. On the other hand, he combined oxide of antimony with different proportions of sulphuret of antimony, and, without any disengagement of sulphureous gas, he obtained *mixtures which may be represented by this formula: oxide + 1 + 2 + 3 + 4, &c. of sulphuret of antimony.* Did he not thus form true combinations, of which some were beautifully transparent? I do not see how *this guards the oxides of this metal from the suspicion of being capable of uniting with sulphur in all doses, and without regard to the invariable laws of proportions*: he must surely admit that these laws are not invariable, and that his apophthegm is limited on the proportions of sulphuret of antimony with the oxide.

401. Sulphur forms another species of combination with the oxides; that which distinguishes these sulphurets is, that when they are subjected to a greater fire than that by which they can be formed, sulphureous acid is disengaged: the same thing takes place as was shown by Proust, when a mixture of sulphur and an oxide is submitted to distillation: a similar product is generally obtained, when a metallic sulphuret is urged by fire with an oxide, and the residue is a metallic sulphuret.

On submitting pyrites to the action of fire,  
Proust

Proust obtained, at the beginning, sulphureous acid and sulphurated hydrogen : he attributes these two substances to the decomposition of water, and he concludes that pyrites is a metallic sulphuret; but the formation of sulphureous acid cannot be owing to the decomposition of water; and these two productions, which he considers as simultaneous, and which are mutually destroyed, cannot be the effect of the same cause: it is probable that the sulphureous acid, which is readily produced by the oxides, is first obtained, and that the sulphurated hydrogen, which alone can be owing to the decomposition of the water, is disengaged afterwards, and that a mutual decomposition takes place when these two substances meet. I therefore draw from Proust's own experiment a conclusion opposite to his: it appears to me to prove, that the iron of the pyrites which he assayed was a little oxided.

Oxide of zinc, treated by fire with sulphur, also produces sulphureous acid, and the metal forms a sulphuret with excess of sulphur: this shows, that if the zinc cannot unite immediately with the sulphur with which it is exposed to heat, the obstacle to the combination does not depend on the absence of a mutual affinity, but on another circumstance, and this is, the volatility of both substances, which reduces them to the elastic state before the force of cohesion is sufficiently weakened for their union to be established.

402. The alkaline sulphurets also dissolve the metals, and even gold, which proves, that if gold cannot combine immediately with sulphur, it is only on account of a circumstance analogous to that which opposes the combination of the zinc: the force of cohesion of the metal does not permit its affinity, which is doubtless not energetic, to produce the combination and retain the sulphur; but, when it is deprived of its force of cohesion, if it can be retained by an affinity which prevents it from volatilizing, the solution can be effected: the alkaline sulphurets can also dissolve the oxides; but these oxides are also reduced to the metallic state by the action of heat.

When the metallic solutions are decomposed by the hydrogenated sulphurets of an alkali, the metal combines with the sulphur, and the sulphurated hydrogen is destroyed, at least in part; because the hydrogen combines with the oxygen of the metal: this decomposition is analogous to that which ammonia experiences with the oxides; but the destructive cause is more powerful in this case, so that the precipitates which are thus obtained, or at least the greater part of them, are metallic sulphurets, and not sulphurets of the oxides, as has been ascertained by Gay Lussac.

I was of opinion, that when a metallic solution was precipitated by sulphurated hydrogen, or by an hidro-sulphuret, the precipitate was a combination of sulphurated hydrogen and oxide,  
and

and that the properties and the differences of several combinations, such as *Kermes mineral* and *golden sulphur of antimony*, might be thus explained; but Gay Lussac has found that the metallic hidro-sulphurets do not exist in many cases in which they are supposed to be, because the sulphurated hydrogen is destroyed in effecting the precipitation, and is reproduced when it is only supposed to be disengaged: he will elucidate this subject in a particular memoir.

I have shown\* that mercury, which is reduced to cinnabar when it is mixed with the hydrogenated sulphuret of pot-ash and ammonia, according to the observation which is principally owing to Baumé, is in the state of a metallic sulphuret in it, and that the sulphurated hydrogen remains in combination with the alkali, so that it does not reduce the hydrogenated sulphurets to pot-ash and ammonia, as is said by Proust; but I had presumed that the black combination, which forms at first, and which is known by the name of *ethiops*, retained sulphurated hydrogen, which the alkali carried off gradually: Seguin has since shown that the ethiops, or black sulphuret, does not contain sulphurated hydrogen, and that it only differs from the red sulphuret in the proportion of the sulphur, so that the mercury passes, in this operation, to the state of red sulphuret, by taking a suitable proportion of sulphur.

† Ann. de Chim. Tom. XXV.

If the red sulphuret is obtained by means of an oxide of mercury, the sulphurated hydrogen of the hydrogenated sulphurets will be destroyed until the oxide acquires the metallic state.

403. The metallic phosphurets, for the knowledge of which we are indebted to Margraf, and especially to Pelletier, appear to be softer, and in general a little less brittle, than the sulphurets: they are more fusible than the insulated metals, and are, at the same time, more combustible when they are exposed to an elevated temperature.

Platina itself is rendered more fusible by phosphorus; and Pelletier has taken advantage of this property to purify it from the iron which it naturally contains, and which alters its qualities; nevertheless, when the greatest part of the phosphorus has been driven off by a strong heat, the infusibility which it regains opposes the disengagement of the remainder of the phosphorus, which has been hitherto an obstacle to the utility of this process: Proust has found phosphorus in the ore of platina.

It is known, that almost all the irons contain phosphorus; if it is in any considerable proportion, it renders the metal brittle in the cold, and impairs the iron obtained from several ores: it appears, that when these ores are passed through the furnace, a mixture of lime favours the disengagement of the phosphorus, by forming phosphate of lime, which remains in the slag: iron retains the phosphorus when it is converted into steel,



steel, which thence participates in the bad qualities of the iron.

Phosphorus having a much greater action on the oxygen of metals, will not combine with the oxides like sulphur, but it reduces them to form phosphurets.

404. Carbon seems to have similar relations with the metals as those of sulphur and phosphorus; but its infusibility most frequently opposes its combination; it, however, exercises an action on iron sufficiently strong to form a well-determined combination with it, whose properties are very remarkable: this is steel. When, therefore, iron is melted, taking care that it is surrounded and covered with charcoal, it dissolves a certain proportion of it, and is thus changed into steel: when bars of iron are cemented, surrounded with charcoal powder, and are kept long enough exposed to a high temperature, they are also impregnated with the charcoal, and changed into steel; so that the art of making steel is reduced to keeping iron in contact with charcoal, at a temperature sufficiently raised, and kept up a long time.

The more the temperature is raised, the greater is the quantity of carbon held in solution by the iron; in proportion as the temperature lowers, the carbon tends to separate, in the same manner as the most fusible metals separate from those which are least so, when the temperature is not sufficient to maintain both in liquefaction (367); but it  
retains

retains some of the metal, so that two combinations separate from the difference of solubility, one with an excess of iron, the other with an excess of carbon. Clouet has proved, by an elegant experiment, that iron could decompose the acid of carbonate of lime, and by that means be converted into steel, while the oxygen of the acid unites to a portion of the metal, and vitrifies with the lime, whose affinity contributes to the effect: Guyton, on his part, has also proved that the diamond changes iron into steel.

By its combination with carbon, of which it always contains more or less, iron acquires properties analogous to those of an alloy of a very ductile metal with another which is much less so; it becomes hard, elastic, and brittle: if the iron made use of is affected with flaws, cracks, and other blemishes, these defects become much more perceptible, and much more injurious, in steel, whose parts solder with difficulty; hence the necessity of employing very pure and well-prepared iron to obtain good steel of cementation.

The qualities of steel depend also on the proportion of carbon: if it dissolves too great a quantity of it, it becomes so brittle that it cannot be used; this may be corrected by melting it with oxide of iron.

Cast iron also contains carbon, and its properties are varied by the proportions; it has also a little oxygen; whence it arises, that it gives less hydrogen gas when it is dissolved by sulphuric acid;

acid\* ; but some properties which have been observed in this gas, lead to a conjecture that it also contains a little hidrogen, in which the carbon of the cast iron, at least of that which is black, is still in the state of charcoal (271) ; this is another difference from steel : an observation of Proust authorizes this conjecture† : he says, that in all solutions of cast iron by the sulphuric or muriatic acids, an oily gas is disengaged, heavy and very odorant, which Priestley had formerly noticed, and called *extremely fetid inflammable air* : he even obtained some drops of oil ; I had not, however, the same result from two specimens of black cast iron which I examined with this view, but there may be differences between them. Another observation leads me to admit of this distinction between the carbon of cast iron and that of steel : Beddoes observed, that when cast iron was converted into wrought iron in reverberatory furnaces, a considerable swelling was at first produced, and the metal was covered with a blue flame, which announced oxycarbured hidrogen : he also obtained an inflammable gas, which has all the characters of the oxycarbured, by exposing cast iron to a great fire in closed vessels‡.

In the analysis of cast iron, of wrought iron, and of steel, there is also found a small quantity

\* Bergman, *de anal. ferri*.—Mém. de l' Acad. 1786.

† Journ. de Phys. Tom. XLIX.

‡ Philos. Trans. 1791-1792.

of silex, whose influence on their qualities is not known.

It has been attempted to ascertain the proportions of carbon by those of the carburet of iron, obtained by means of the solution in sulphuric acid; but a portion of this carburet is destroyed, and the carbon passes in combination in the hydrogen gas; this effect takes place principally when the solution is made with vivacity and by means of heat: for the black precipitate, which is formed at the commencement, frequently disappears: to avoid this inconvenience, Vauquelin employed sulphureous acid; but the property which iron has of decomposing a part of the sulphureous acid, by taking the sulphur from it, renders this analysis difficult and even uncertain: I am of opinion, that at least comparable results may be obtained by making the solution with sulphuric acid, sufficiently diluted with water, that its action may be slow and very moderate, and by adding the acid in portions, until the solution is completed.

405. Platina lets fall a black powder by dissolving, and when this solution is precipitated by another metal, by zinc, for example, as was done by Bergman \*, a considerable quantity of this powder also precipitates: a solution of 100 parts of platina, precipitated by zinc, gave 77 of

\* *De cob. nick. plat. et mag.*

it. Tillet also obtained a considerable quantity of this black matter, by precipitating the solution of copper and silver in nitric acid, with copper\*. Bergman observed, that great part of this substance exhaled in smoke, when he tried it with the blow-pipe, and that it was not affected by the magnet, even when it had been calcined: Tillet obtained only a very small quantity from platina, and the rest entirely disappeared in his assays by the cupel. These facts seem to announce that this substance is a carburet of platina, and that the carbon is not only found in great proportion in the platina before its solution, but that it can enter into the solution in a considerable quantity, and without giving any indication of its existence until it is precipitated by a metal, unless the deep colour of the solutions of platina are attributed to it.

Proust has lately published some very interesting observations on this substance; but he has only noticed what separates when its solution is effected: his experiments prove that this substance contains the phosphuret and sulphuret of platina; after having treated it with nitro-muriatic acid, nothing remained but a black powder, which he compared to plumbago; but this contains iron, and it appears that the other substance only contains a very small quantity of platina. Is

\* Mém. de l'Acad. 1779.



the precipitate obtained by the processes of Bergman and of Tillet, of the same nature as that which has been examined by Proust? It is greatly to be desired that this subject should occupy a little more of this intelligent chemist's time.

## APPENDIX.

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### *On Vegetable and Animal Substances.*

THE products of vegetation are composed of the same substances as those of which we have noticed the chemical action, but particularly of those whose elasticity is compressed by the combinations which they form : this composition renders them liable to undergo alterations with facility (187), not only from the action of other substances, but also from the reciprocal action of their own elements, and from variations of temperature.

Nevertheless, their formation and the spontaneous changes which they experience, do not suppose either other affinities, or other principles of action, than those which produce chemical effects : we may be the more convinced of this, because we can form substances of a vegetable nature, such as the oxalic acid, the acidulous oxalate of pot-ash, the malic and acetic acids, in every respect similar to natural productions ; this arises from employing no means in our laboratories which are different from those of nature : the cir-

VOL. II. cc cumstances

cumstances which favour the exercise of the properties possessed by each substance are only united : nature enjoys its power from these immutable properties alone ; the particular views which are attributed to her, the methods which are devised for her, only mislead observation from the true causes, to which ideal ones are substituted, whose magic is so much the greater as it is enveloped in a darker cloud.

If a chemist is unable to unite the circumstances necessary to some productions, if even he is unacquainted with them, there are also a great number of combinations which can only be formed by his care ; thus alcohol, ether, rectified animal oil, lime, barites, cannot be met with in natural productions.

Even though the causes of these productions might be unknown, chemistry still retains the knowledge of the succession of changes which are effected in them, the origin of the substances which serve for their reciprocal formation, the influence of the circumstances which can favour or prevent it : it seeks the analogy between each of these objects, and such others as can be submitted to an exact analysis : it forms conjectures on the means which may produce any result, and compares them with those which experience has shown the use of, in other circumstances : thus it prepares the ulterior steps of observation, which rectify the first attempts, give other indications, and successively extend the limits of the art.

In

In this manner chemistry has lately been applied to the phenomena of vegetation ; it has already acquired important determinations, which, by uniting with the study of the organization, which has been cultivated with equal success, form that elegant part of natural philosophy called vegetable physiology.

I shall offer a summary, or rather an outline of the knowledge which chemistry has given on this still new subject : it would not be easy for me to produce well established opinions, and I shall not engage in the discussions which they would require ; my only object is to compare the products of vegetation, and the forces which are brought into action in it, with other substances, and other causes of chemical phenomena. I must also confess that I have not attended much to these inquiries : the few ideas I offer must therefore be considered as opinions necessarily conjectural in themselves, and but little investigated by their author.

After a sketch of the phenomena of vegetation, beginning with germination, which opens the scene, I shall proceed to the differences of composition which distinguish vegetable substances, the changes which they experience from their reciprocal action, from that of other substances, and from variations of temperature.

Senebier and Hubert observed that seeds could not germinate in azote or hidrogen gas \* ; but that

\* Mém. sur la Germin. Phys. Végét. Tom. III.

they sprouted in oxygen gas (and then carbonic acid was produced), or in a mixture of oxygen gas with either azote gas or hydrogen gas; in the last mixture the hydrogen gas takes the carbon, and is changed into oxi-carburated hydrogen; so that then it is not carbonic acid which forms, but a ternary combination of hydrogen, carbon, and oxygen (287).

Gough\* and Rollo† also found that germination could not take place without the contact of oxygen gas, and the experiments of Woodhouse‡ confirm this result. The two first observed that, by means of this production of carbonic acid, cereal substances became saccharine, as is seen in malt. Gough particularly remarked that when this effect of germination did not take place from a deficiency of oxygen, an inflammable gas and carbonic acid were disengaged from the humected grain, which entered into putrefaction, and which, consequently, lost the property of germinating; that this effect was the more rapid as the temperature was more raised, and that the seeds differed in their disposition to putrefy, so that some lost the property of germinating much more readily than others; but they both thought that the oxygen gas was partly employed in forming carbonic acid, and that it partly entered into the composition of the saccharine substance.

\*. Bibl. Brit. Tom. XI.

† Ann. de Chim. Tom. XXV.

‡ *Ibid.* Tom. XLIII.



T. de Saussure has proved that the carbonic acid which is produced in germination, is owing to the combination of the oxygen gas, by whose contact it is effected, since the volume is not sensibly altered, and since the oxygen which is afterwards deficient in the residual air, is equivalent to the portion which must have entered into the composition of the carbonic acid \*.

From what precedes, it results that in germination or in the commencement of vegetation, carbonic acid is produced, of which the carbon arises from the seed and the oxygen from the atmosphere, which must be in contact with it: by this a saccharine substance is formed in the seed which serves for the progress of vegetation but does not add to the oxygen which enters into combination.

Some seeds, peas, for example, can experience a commencement of germination under water, and without the contact of air; then carbonic acid is disengaged which proceeds wholly from their substance: but the germination soon ceases, and putrefaction takes place.

Senebier compares this first act of germination to fermentation. I do not agree with this learned philosopher, if he makes the comparison with the vinous fermentation: for this, the saccharine substance must be formed, and this is so true, that the cereal seeds do not become fermentescible un-

til they have become saccharine by germination, whose different effects must precede those produced by it: it is by the action of oxygen gas that the seed is freed from its carbon in germination; it is by the action of the ferment on the saccharine substance that carbonic acid is produced in vinous fermentation, as we shall see.

When the seed has sprouted and the plant vegetates, the phenomena are different; light becomes necessary to the plant, and without it, it etiolates, the green substance is not formed, or at least is so only in a very small number of circumstances.

In the observations on the effects produced in vegetation by light and darkness, different results will be found; they, however, seem to agree in the effect of the privation of light: the air in which the vegetation is then effected, is vitiated, so that the proportion of oxygen is diminished in it, as was shown by Ingenhouz; and T. Saussure has proved that this effect depends on a part of its oxygen being employed to produce carbonic acid, which, in this case, is not decomposed.

It is generally admitted, since Priestley introduced this species of observation, that the air in which vegetation is effected with the influence of light, receives a greater proportion of oxygen; but most of the observations have been made by keeping plants under water, and then the effect which the light produces on the water may be blended with that which arises from the plant.

Rumford

Rumford has shown\* that raw silk, cotton, and other substances, by being exposed to light, in water, occasioned the disengagement of a certain quantity of oxygen gas, though slowly, and particularly when the green matter and microscopic animals were produced in it; now this last circumstance is sufficient for the disengagement of oxygen gas. Woodhouse replies, that plants give it too quickly to attribute it to this cause; it is, however, probable that it contributed to the products which were obtained without this cause of error being suspected.

Senebier found that plants exposed to the sun, in water which had undergone ebullition, did not yield oxygen gas. This observation shows that the oxygen gas disengaged from vegetables immersed in water, must not be attributed to the plant alone; but it should not be inferred that none is disengaged from them, for water deprived of oxygen gas would retain that which might arise from them. Spallanzani also observed that the effects of vegetation on the air varied, when they were examined by immersing the plants in water, or by keeping them in the air; he only obtained a dilatation of the air with some plants, and then he generally gained more oxygen†. One cause of this difference has been discovered, and it has been ascertained that the proportion of oxygen gas

\* Philos. Trans. 1787.

† Journ. de Phys. An VII.

is constantly increased in the air in which vegetation is performed, with exposure to light, when the air or the water in which the plant is, contains carbonic acid ; but with other conditions the results are different.

We are indebted to Senebier for the important discovery of the decomposition of carbonic acid by vegetation, and of the disengagement of oxygen gas arising from it. By this, the origin of the carbon which is fixed in plants when they grow in water, and are insulated from every substance which could afford it to them immediately, is learnt. T. Saussure has determined the circumstances of this decomposition by very accurate experiments made on peas. He has shown that the carbonic acid is decomposed, and that the proportion of oxygen gas in the air is augmented ; but that, without the carbonic acid, the state of the air in which the vegetation is performed, does not experience any change in the light, and that, in the dark, it loses oxygen in the ratio of the carbonic acid which forms, but which does not experience decomposition, so that, then, the proportion of the oxygen is continually diminishing.

If all plants exercised a uniform action, it might be concluded from the latter observations that the air acquires a greater proportion of oxygen by the action of light, only by means of the decomposition of the carbonic acid in the air or in the water with which the leaves are immediately in contact ;

contact ; but this conclusion does not invalidate the decomposition of the water which rests on other proofs.

All vegetables contain more or less of oily and resinous substances ; the colouring part itself, which is produced in vegetables exposed to light in pure water, has a resinous character : now in the composition of every oily and resinous substance there is a proportion of hidrogen, much greater than in water, since water is partly the result of the combustion of this substance, that is to say, of its new combination with oxigen : a decomposition of water must therefore always take place to give rise to substances of a resinous character when the vegetation is performed without the concurrence of foreign bodies.

Saussure observed that peas vegetated in atmospheric air, contained within an insulated space, whether the air was taken in its natural state, or had been previously washed with lime-water, without its volume being diminished or its purity changed ; nevertheless, when he left lime in the apparatus, it took the carbonic acid, and vegetation ceased. Hence he concluded that a little carbonic acid is really then formed, although it is not perceptible by examining the air, but that it is again taken and decomposed by the vegetable, and that without this successive decomposition, vegetation could not subsist.

But so far from it being possible to infer that the water is not decomposed at the same time, it seems



seems to me that this observation itself proves the contrary; for the atmospheric air had not changed its state, and nevertheless the mean term of the increase which each small plant had acquired in the space of ten days, was eight grains, which cannot be attributed to the carbon or to the decomposition of the carbonic acid, and the green parts were formed: there must, therefore, have been a decomposition of water; its oxygen must have entered into one combination, while its hydrogen was fixed in another.

Still there is a production and decomposition of carbonic acid, but in such a way that what is formed only counterbalances what is decomposed: if these two effects cannot be produced, the vegetable perishes.

Hence it may be concluded, that in the preceding instance the increase acquired by the vegetable is particularly owing to the decomposition of the water, but that this decomposition does not take place, unless there is at the same time a decomposition of carbonic acid in one part of the vegetable, while another part gives carbon to produce the same acid.

It therefore appears to me probable, according to the explanation given by Fourcroy in the *Encyclopedie methodique*, that the action of carbon on the hydrogen contributes to the decomposition of the water and carbonic acid, and that it is necessary to effect this double decomposition: it is thus that a sulphuret decomposes water which  
would

would have resisted the separate action of the sulphur and alkali.

Is it to the small quantity of carbonic acid found in the sap, that what serves for the immediate support and growth of the vegetable substance must be attributed? The experiments of Saussure indicate that it is not; for the branch of a plant in the ground offered no difference with the peas which grew in the water. The sap undergoes multiplied elaborations before it forms the peculiar juice which is received by the leaves: this juice should be examined in this point of view.

It appears to me, therefore, that the observations which have been hitherto made, prove, that the carbonic acid and water are decomposed by means of the action of light and the reciprocal action of the carbon and hydrogen; that this decomposition is perfected in the leaves exposed to the sun; that the oxygen is frequently disengaged, and that sometimes it remains in combination: but we are still unacquainted with the state to which the carbonic acid and water have arrived in the leaf in which their decomposition is finished.

The experiments which have been made, prove, indeed, that carbonic acid may serve for the growth of a vegetable, and that a certain portion favours this effect; but they were all executed by keeping the plants or their roots in pure water, or in that which did not contain carbonic acid: the action of atmospheric air on manures has also been observed, and it was found that they formed carbonic

bonic acid ; but these observations do not prove that the roots of vegetables receive only carbonic acid when they grow in the open earth.

Hassenfratz was of opinion that the substances which favour vegetation contribute to it, because they supply it with charcoal rendered soluble, and Kirwan has adopted his opinion : on the other hand, Senebier, who has shown that carbonic acid was capable of supporting vegetation, and who found that dunghill-water produced bad effects, concluded that all the charcoal which accumulates in vegetables, arises from the carbonic acid which they receive from the atmosphere and the water, or which is produced by the manure.

This conclusion is perhaps too general, or too premature : it appears to me to require more numerous and more exact experiments to prove that every substance which favours vegetation as a manure, serves only to produce carbonic acid : it is also known that several colouring substances can penetrate beyond the roots without losing their quality, and that consequently substances containing charcoal may enter into plants and supply them with nourishment, without having passed into the state of carbonic acid ; the observation of Saussure which I have quoted, seems to prove that the carbonic acid which enters by the roots is not the same as is decomposed in the leaf.

Whatever it may be, the vegetables which grow and succeed on shelving soils where animals cannot carry the principles of reproduction, and which  
also

also experience, from the running off of rain-waters, a loss of the substances formed by the vegetation, can only receive carbon and hydrogen from the decomposition of carbonic acid and water, whether they are produced immediately by the vegetation, or the substances which have first resulted from it have passed into other combinations, and have served as manure for the latter vegetation.

Although azote may be considered as an element peculiar to animal substances, and which serves to give them their distinctive character, it is nevertheless indubitable that it enters into the composition of several parts of vegetables, even when they only owe their growth to the decomposition of water and carbonic acid : thus Rouelle has shown, that when the expressed juice of herbaceous plants was exposed to the fire, the fecula, which coagulates by the action of heat, as well as by that of alcohol, contains a substance which has the properties of animal matters ; but it appears to be chiefly when plants approach maturity that the azote is fixed in them, and that light is favourable to its production ; for, according to an observation of Proust \*, etiolated plants contain much less of it than those which have become green.

It is not known how this azote penetrates vegetables to enter into their composition, but it

\* Journ. de Phys. Tom. LVI. p. 107.

may be introduced with the water, which always holds some in solution, and which is absorbed in so great a quantity in vegetation: the opinion, that it is necessarily associated with the carbonic acid, seems to me to be unfounded; this may be entirely deprived of it, although it favours its disengagement from the water which contains it.

The observations made on the earths found in vegetables, prove that they are in much greater quantity in herbaceous plants than in the ligneous, and in these than in the trees; and the experiments made by Saussure \* on the ashes of plants which had vegetated on the summits of some mountains, in different soils, appear, from the correspondence he observed between the parts of the earth on which the plants grew, and those which compose the ashes of these plants, to prove that magnesia, alumine, and silex are not the work of vegetation, but proceed from the soil, and that they are only found accidentally in vegetables: we can only be undecided with respect to calcareous earth; nevertheless, the observations of Bergman and Senebier, on the quantity which can be furnished, even by rain-water, render it at least very probable that it is equally foreign to vegetation: this is particularly applicable to the iron and manganese which is found in ashes. The earths introduced into vegetables

\* Journ. de Phys. Tom. LII.



may be distributed through them, and contribute to their organic effects; but silex seems to experience a weaker action of combination in them than the others, since it unites and forms a species of crystallization in the tabasheer, as was observed by Macie\*, and is, in great part, driven to the epidermis in rushes and gramineous plants, as is evident from the observations of Davy†.

It is also probable that the salts which contain a mineral acid are only introduced into vegetables: soda is obtained in abundance in some plants which grow on the sea-shores, while the same plants do not yield any when they grow in soils remote from the salt water, and according to an observation which I have from Cels, those which do yield it on the borders of the sea, which are not too wet, contain only muriate of soda when they grow in the salt water itself: these considerations induce me to believe that the soda of plants arises from the muriate of soda, which is decomposed by the union of the conditions which produce this decomposition in other circumstances (225).

Pot-ash is found much more generally in plants, and its origin is not yet known; there is this remarkable fact in the observations of Saussure, that pot-ash is found in greatest proportion in the

\* Philos. Trans. 1791.

† Nicholson's Journ. 1789.

ashes of vegetables which have grown in a calcareous soil; on the other hand, herbaceous plants contain more than those which have a closer texture: until the result of more positive observations is obtained, I am led to believe that pot-ash is not the work of vegetation, because all the phenomena offered by vegetation indicate that its effects are only owing to causes which act slowly, to forces which are nearly balanced, so that a small reduction of temperature is sufficient to suspend them, and that products should not be looked for which require energetic agents.

One part of the materials, in common vegetation, must arise from the earth and enter into the composition of the sap; but this, in the state in which it is obtained from trees, has been subjected to an elaboration. We are indebted to Vauquelin for some very interesting observations on the sap\*: he found acetate of pot-ash and acetate of lime in it; and in that of some trees, acetic acid in excess, but it was principally in the sap which is first in motion; what succeeds does not contain any, or contains much less, and since he discovered these substances in the soil, it may be presumed that they are taken from the earth as well as other saline substances, and are destroyed by the prolonged act of vegetation: the different saps, however, yielded him other sub-

\* Journ. de Phys. An VII.

stances, which can only be attributed to the work of vegetation : thus the sap of some trees yielded him tannin and gallic acid ; that of the birch contains a considerable quantity of a saccharine substance, but no tannin or gallic acid ; all have a greater or less quantity of a substance which yields ammonia and contains azote.

The sap takes a more decided character when it forms the proper juice of the plant, such as turpentine : this is seldom found in the stem, unless in the bark, or the part which joins to it, it has generally a particular character in the leaves, in the fruits, and in the other parts of the plant : it does not follow the direction of the sap ; for, when a portion of the bark of a cherry tree is removed, the mucilage flows through the upper part of the section ; and when an incision is made in a branch of fir, the turpentine issues from the part nearest to the small end, even when the branch is bent towards the earth \*.

Thus the juices which penetrate into a plant change their properties continually as they proceed, and are distributed to the different parts of the stem, the leaves, and the fruits.

These changes are owing, 1st, to the reciprocal action of substances, which, containing elements naturally elastic, experience modifications from the slightest causes ; they become more stable as they attain to a combination in which the

elements can exercise their reciprocal action, and undergo a proportionate condensation: thus substances are formed which acquire a peculiar existence, and which are sometimes wholly insulated from the others: it is in this manner that the stem, become ligneous, only increases by more pliant prolongations at its surface, or at its extremities; that gums or resins transude; and that the acids or their combinations become fixed in some parts.

The substances, therefore, which tend to take the solid state, and which are on the verge of existence, will be solicited by this tendency itself to form, and the elements possess a disposition to produce the combinations in which the reciprocal condensation is greatest.

2d. To the action of the organs which contribute particularly to the transmutations which they effect, when they are limited to the small space they occupy; for example, the juices take very different properties at the petiole of leaves and the pedicle of fruits: on this depends the utility of grafting.

Although the action of the organs is obscure, and, hitherto, few experiments have been made which can lead to a knowledge of what it consists in, we may, however, form some conjectures, and compare its effects with those whose causes are better known.

It may be observed, that solid substances exercise an action on the liquids by which they tend to

to give their constitution to the substances which are held in solution, while those which are liquid tend, on the contrary, to maintain the liquidity of such as have the greatest disposition to preserve this state (29).

If this action produces considerable effects in capillary tubes, how much greater must they be in very small ones greatly multiplied, and especially when they are formed of *moleculæ* which have little tenacity, and, consequently, the reciprocal affinity scarcely weakens the tendency to combination !

The juices which run through these vessels are, themselves, composed of substances very unstable in their composition, and they usually contain some whose solution is imperfect, so that they are milky, or particles, which appear to be insulated, are distinguishable by the microscope : now these particles, being weakly held in solution, do not oppose any resistance to the forces which tend to modify them, and we shall find a striking example of this action in the phenomena of fermentation.

This action of the solids concurs with the disposition of the elements of a combination to unite in proportions in which their reciprocal action produces the most condensation, and with the effects of light and air, which operate on some particles, while others are deprived of its influence.



The seed therefore begins, by means of the action of the air, to free itself from the carbon which opposed the reciprocal action of the two substances of which it is principally composed; thus a saccharine matter is produced, which, having acquired solubility, can exercise an action on the vegetable rudiments; this action is directed on them and on the glutinous part, the concurrence of light becomes necessary, carbonic acid is continually formed, which, afterwards, produces a mutual decomposition with the water; the oxygen, carbon, hidrogen, and azote, are so distributed, that one of the elements frequently predominates in one of the products, while another gives its character to another compound: some substances, on the contrary, are formed which maintain an equilibrium of action between their elements, or are in a neutral state.

The changes which take place in fruits are independent of vegetation: Ingenhouz has observed that they are decomposed by the air; they produce carbonic acid, even when they are exposed to the light.

It appears, therefore, that they experience a change analogous to that which produces germination in seeds; they lose a part of their carbon, and thus their juice becomes saccharine instead of harsh which it was from the operation of vegetation. With respect to the petals and leaves which degenerate, they also produce carbonic acid; but  
then

then it is another species of decomposition which is effected.

The products of vegetation differ in the elements which compose them, in their proportions, and in the predominating qualities which they retain and are distinguished by: in some the properties of oxygen gives them their character, these are the acids; in others it is those of hydrogen, such are the oils and the resins; others owe their characteristic properties to azote, by this they approximate to animal substances, and putrefy like them; several are found in a state of combination which does not permit any of their elements to appear superior, so that they seem to experience a saturation nearly complete; in this class are the gummy substances, starch and sugar.

None of these substances, of which several subdivisions may be formed, established on greater or less differences, exists without the union of oxygen, hydrogen, and carbon, and there are some, such as sugar, starch, and gum, which do not contain azote; but this is found in a greater or less proportion in the others, and even in some acids: we have seen that the tartareous acid contains it (327), and it results from the observations of Proust\*, that there is also a certain quantity in acetic acid.

It cannot be strictly inferred from the characteristic properties of a vegetable substance that it con-

\* Journ. de Phys. Tom. LVI.

tains a greater proportion of one element than another, in which the properties of the elements are in a state of neutralization; for if hidrogen, for example, is in a certain quantity, it produces a much greater saturation of oxygen than carbon does, as is obvious from a comparison of carbonic acid with water (262).

It is difficult to form a judgment from the results of the analyses which have been hitherto made; it is to be wished that chemists would turn their attention to this subject with the same anxiety as they manifest to determine the composition of mineral substances: the carbon and azote may be estimated with accuracy; there is more difficulty in avoiding uncertainty as to the oxygen and hidrogen.

Sugar, according to Lavoisier, contains 64 parts of oxygen, 28 of carbon, and 8 of hidrogen: in this valuation he has neglected the carbon which enters into the composition of the carbonic acid, and of the oxi-carburated hidrogen gas disengaged in the analysis of sugar; by including them I have found that the quantity of carbon should be raised to nearly 0.33, but since the charcoal retains hidrogen, it appears to me that Lavoisier's estimate may be admitted as a satisfactory approximation. Fourcroy and Vauquelin found that 100 parts of gum contain 23.08 of carbon, 11.54 of hidrogen, and 65.38 of oxygen\*: to 100 parts of oxalic acid, they appro-

\* Syst. de Conn, Chim, Tom. VII.

priate 77 parts of oxygen, 13 of carbon, and 10 of hydrogen: I must be permitted to have some doubts of the latter analysis: the sugar must be deprived of part of its hydrogen in passing to the state of acid by the action of the nitric acid, for the hydrogen combines with the oxygen from preference, particularly when the combination does not take the elastic state, which is readily perceived in the action of oxygenated muriatic acid, which produces the effects of a slight combustion on the sugar: now, according to the analysis of Lavoisier, which they admit, and whose results seem to me to come very near the truth, sugar has only 0.08 of hydrogen.

However this may be, it will be seen from the analysis which I have just quoted, that the acids, less energetic than the oxalic, cannot have a greater proportion of oxygen than sugar and gum, although these have no acid property.

The solidity or softness, the solubility or insolubility, of vegetable substances, cannot be deduced from those of the parts which compose them, because the condensation which their elastic elements undergo, varies the proportions sufficiently to change their dispositions in this respect.

Hence a greater quantity of earth is not the cause of greater solidity: herbaceous plants give much more ashes than hard woods. In like manner, the quantity of carbon does not correspond with the greater hardness: woods yield only a fifth

fifth part, nearly, of their weight in charcoal, while sugar and gum leave much more, and that of the gall-nut exceeds the third of its weight. Chaptal† remarks, that fecula, digested in nitric acid, takes properties which approach to those of ligneous substances; that the cellular texture, which is immediately covered by the epidermis in vegetables, takes a ligneous character by the action of the air; and that trees acquire greater hardness when they are stripped of their bark; and he attributes the greater solidity acquired in these circumstances to the combination of oxygen. Jameson‡ has confirmed these conjectures by the effects which weak nitric acid produces on starch. In fact, wood gives much acid in its distillation. This oxidation is analogous to that of indigo, which acquires insolubility by combination with oxygen, and which admits of solution in the alkalis when it is deprived of it.

The substances which are blended under the name of extracts, experience rapid changes by the action of the air, by that of water and of alcohol, and by the heat which they are subjected to in their solution, as is seen in the excellent analysis of quinquina\*\* for which we are indebted to Fourcroy. These different means easily produce

\* Proust, Journ. de Phys. An. VIII.—Elem. de l'Art de la Teinture, Tom. I.

† Elem. de Chim. Tom. III.

‡ Bibl. Brit. Tom. VIII.

\*\* Ann. de Chim. Tom. VIII. and IX.



separations and new combinations which did not exist: so that great circumspection is necessary in determining what was the natural state of the substance under examination, from the products which are obtained by these means.

By the action of the air, the volatile oils take the properties of resins, and lose their volatility, either because oxygen combines with them, or, principally, because that part of the hydrogen which adheres least to them, separates and forms water: but a brisk action is produced between some substances, which quickly changes their properties, and which deserves a particular attention for the light it can throw upon the reciprocal action of vegetable substances, even in other circumstances, and upon the processes of one of the most useful arts of society: I speak of the vinous fermentation.

The theory of this fermentation should determine what are the substances necessary to its establishment; what are the results of the mutual action of these substances; and, in what it consists.

Chemists long confined themselves to the appearances of the vinous fermentation; they only perceived in it an intestine movement which attenuated and divided the gross particles, disengaged heat, and changed the phlogistic state of it; they neglected the first object, which should have preceded their reasonings, the determination of the substances whose reciprocal action produced the fermentation;

fermentation ; or if they admitted a ferment, if even they misapplied the idea of a ferment, they considered this intermedium only as the exciting cause of the intestine motion, but they left it undetermined.

The progress of the system, caused an inquiry into what the substance was which could direct its action on the saccharine matter, which was discovered in what was subjected to fermentation : experiments seemed to indicate that it was an acid : Henry and Bullion were induced to form this opinion. The latter however perceived that another intermediate substance, whose nature he could not discover, was wanting.

Fabroni obtained a prize, offered in 1785 by the *Académie Economique* of Florence: he proved\* that the expressed juice of grapes deposits a sediment ; that this sediment forms a fifth of the volume of the liquid ; that when the fermentation is completed its apparent volume is diminished one third ; and, that at a low temperature the juice is entirely clarified by depositing this substance : nevertheless it retains some of it in solution, and can still ferment at a suitable temperature.

He succeeded in the perfect separation of the sediment, by repeated filtrations through thick and fine papers, but he announces that he had previously rendered it more glutinous by means of a strong heat, to which he exposed it a few seconds. The

\* De l'art de faire du vin, par Fabroni.

must prepared in this manner cannot ferment, but the sediment mixed with a fermentescible substance causes it to enter into fermentation.

If the must is placed on the fire, it scarcely attains the mean degree between ice and boiling water, when it becomes like a matter almost coagulated, and the sediment is disengaged in the form of scum.

Some others of Fabroni's experiments prove that the glutinous part of wheat produces, either on the must deprived of its sediment, or in an artificial preparation, the same effect as the sediment of the must, except that the fermentation is more slowly established, and requires a higher temperature and the concurrence of tartar; it shows that the leaves and their juice may also be used, since a substance similar to the glutinous part, but liquid, is found in them, as has been proved by Hilaire Rouelle: he observed that the flowers of the elder could excite fermentation on account of containing this substance.

Fabroni says "That which particularly contributes to prove that the rapid movement of fermentation is owing to this vegeto-animal substance, is that it principally constitutes the scum of wine and beer which ferment; a substance in which resides the faculty of bringing the bodies it is mixed with, to a quick fermentation: he adds, we find from Pliny, that this faculty was not unknown to the ancients."

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He did not discover this property of exciting fermentation in strong glue, in the albumen of the egg, or in the indissoluble part of the animal fibre.

Fabroni's work is preceded by an anatomical examination of the grape, and he shows that it is composed of different liquid substances which are separated by membranes ; that the saccharine substance is chiefly found between the centre and the bark ; that it sometimes forms small saccharine crystals there ; and, that the vegeto-animal substance resides principally in the membranes : it results from this important observation that grapes, and Fabroni applies it to other fruits, cannot undergo fermentation until the matters whose reciprocal action produces the fermentation are blended and mixed by pressure and trituration.

His inquiries are confused with many considerations drawn from the hypothesis of phlogiston, which prevent him from deducing the consequences which his observations offer in their simplicity, and notwithstanding their results, he endeavours to introduce the action of an acid, which may sometimes be a useful agent, but is not necessary, and of which he ought, at least, to have distinguished the particular action : this excellent philosopher has corrected his opinions in a memoir which he presented to the Philomatic Society, during his residence in Paris, for an extract from which we are indebted to Fourcroy\*.

\* Ann. de Chim. Tom. XXXI.

From this extract it will be seen that Fabroni no longer considers the acid as an indispensable agent of fermentation, and that he has brought his explanations to a greater simplicity: "the  
" saccharine matter is the element necessary to  
" the vinous fermentation; it is decomposed in  
" it; it only ferments by the action of another  
" substance, capable of re-acting upon it, and  
" of disengaging an elastic fluid from it.

" The matter which decomposes the sugar in  
" the vinous effervescence is the vegcto-animal  
" substance; it is seated in peculiar utricles in the  
" grape, as well as in the grain; by crushing the  
" grape this glutinous matter is mixed with the  
" sugar, as if an acid and a carbonate were poured  
" into the same vessel; as soon as the two matters  
" are in contact the effervescence or fermentation  
" commences in it, as happens in every other operation of chemistry. . . . .

" When these matters are liquid, the carbon of  
" the glutinous part attacks the oxygen of the sugar, it burns and is disengaged in gas; the  
" sugar, partly deoxidated, forms a new kind of  
" combination with the hidrogen and azote."

Thenard has made similar observations on the juice of the gooseberry, of the cherry, and of several other fruits, so that it may be considered as constant, 1st, that the expressed juices of fruits, which are capable of the vinous fermentation contain a saccharine substance, and a vegcto-animal substance:



substance: 2d, that the substances are insulated from each other in the fruit which contains them: 3d, that, as soon as they are brought together and blended by expression, their reciprocal action begins the phenomena of fermentation: but here different questions offer themselves; is this vegeto-animal substance, which serves as a ferment, a uniform substance? Must it be in a state of solution to exercise its action? Can another substance, such as the tartar, promote this action? It results from the experiments of Fabroni and Thenard, that the vegeto-animal matter contained in fermentescible juices is similar to the yeast which separates from wine and beer in fermentation; but the first has shown that the glutinous part of wheat is also capable of exciting fermentation, though it is then slower and requires a higher temperature: I have produced fermentation in a mixture of sugar and gluten by adding a little tartar to it, so that the gluten can perform the functions of yeast, although less perfectly; this difference appears to me to depend only on the greater adhesion of its particles, which opposes its action on the other substances, and by employing a gluten whose tenacity was destroyed by incipient putrefaction I found that the fermentation was established more readily. In analysis and in the disposition to putrefaction there is but little difference perceived between gluten and yeast; nevertheless Hilaire Rouelle obtained a little acid from yeast, at the commencement

commencement of its distillation, a product which he did not get from gluten\*. This difference is to be attributed to a portion of starch, which separates with the vegeto-animal substance, for he did not obtain any acid from the coagulated gluten of herbaceous juices, and Fabroni has proved that these may be substituted for yeast.

The ferment is therefore a vegeto-animal substance, or its composition has some analogy with that of animal substances, and it may have some differences in its properties, which render it more or less proper to produce fermentation.

Seguin, who undertook an extensive course of experiments, principally directed to the perfection of the different arts which have fermentation for their object, observed that yeast digested with warm water formed a solution which had, afterwards, the property of fermenting with sugar, while the ferment of fruits coagulated by the same heat. Yeast which I boiled with water for ten minutes fermented with sugar, but much slower than in its ordinary state ; it is the same with that which has been kept in digestion with alcohol ; finally, that which has been strongly dried also ferments much slower, so that this substance itself is capable of modifications which change the qualities of the ferment.

It is the same with the saccharine substance, although it is compared with sugar. Yeast and

\* Tableau de l'Anal. Chim.

sugar should be taken for the types of two substances which act in fermentation like an acid and an alkali, of which several species exist in the theory of saline combinations: Proust has also established\* a difference between the sugar obtained from the must of grapes by crystallization, and common sugar; these differences will also produce variations in the result of the fermentation: the saccharine substance of the must of beer resembles that of the must of wine only in its general properties.

If, when the fermentation has become brisk between the sugar and the yeast, the liquor is filtered, it passes transparent, and all the fermentation ceases or is suspended; it recommences as soon as the ferment is again mixed with the saccharine solution; nevertheless the filtered liquid at length becomes a little turbid; it forms a small deposit, and a fermentation is slowly produced which has but little activity. In fact, that which can pass in a limpid solution, must, from that cause, be subject to a force of combination which opposes its change of state, or which renders it slow and successive, instead of that strong and tumultuous action which characterizes the vinous fermentation. It might be supposed that the solution of the ferment of which I have spoken is produced by the action of the sugar; but Seguin ascertained that water put to the ferment produced the same

\* Journ. de Phys. Tom. LVI.

effect, by dissolving sugar in it after its separation, as when the mixture of sugar and ferment was filtered after they had remained together, so that water alone dissolves as much of the latter, as when it holds sugar in solution at the same time.

Several experiments of Fabroni and Bullion seem to prove that tartar is favourable to fermentation; but since it is not a necessary ingredient in it, it probably acts only on the vegeto-animal substance. It is known that the vegetable acids can dissolve gluten, and the acidulous tartar seems to have this property in particular: gluten mixed with sugar and water gave me very doubtful indications of fermentation: but by adding tartar to the amount of one-fifth of the weight of the gluten, the liquor became vinous, although the fermentation was much slower, and required a higher temperature than with yeast; thus, though further experiments are requisite to determine how far the tartar may be useful, it is probable that it serves to diminish the insolubility of the ferment. Is it by the tartar, or another acid, or by the glutinous part, that the stalk of the grape contributes to fermentation?

When, at a temperature sufficiently elevated, the ferment and saccharine substance have been blended by the expression of the grapes, as well as by the pressure or trituration of other fruits, a spontaneous movement is almost instantly perceived to be produced by their reciprocal action, the carbonic acid gas which is disengaged agitates

the liquid, and Fabroni compared this phenomenon to effervescence with reason; the cause and effect of them are the same: the saccharine substance loses its sweet taste; the liquor acquires greater specific lightness, and becomes vinous; the intestine motion, and the bubbles of carbonic acid which attach to the solid parts, throw them to the surface in the form of scum; a great part of the ferment is in it, and if the scum is suffered to run off, or if it is separated, the fermentation may cease before the saccharine part has undergone fermentation; one method of reviving it when it languishes is to renew the mixture by motion or by pressure (*foulage*).

When the fermentation has lost its vivacity, the liquor which was turbid becomes clear, the heterogeneous parts are deposited: great part of this sediment is the superfluous ferment.

Nevertheless, the clear wine continues to experience a change, much slower, and which sometimes lasts for years; by this its qualities attain perfection to a certain point, and it becomes more spirituous. During this slow action it still deposits ferment, which forms a great part of the lees, probably because this which was liquid is coagulated by the action of the liquor, now become more spirituous. The analysis of the lees, which is deposited successively, proves that a great part of it is composed of the vegeto-animal substance, for Rouelle obtained much ammonia from it, and Proust also compared it to animal substances.

We



We have remarked before that when a mixture of sugar and yeast is filtered, the fermentation, though brisk, is suspended, but that at length a slow and inactive one is established: it seems, therefore, that in this artificial fermentation, as well as in that of the must of grapes, all that part of the fermentation, to which this name is more especially given, and which precedes the clarification, is owing to the action of the ferment which is not in solution, so that the turbid state is a necessary condition of the fermentescible juices.

Lavoisier made experiments on the products of the fermentation of sugar and yeast, with his accustomed precision: it results from them that 100 ponderable parts of sugar consume only about  $\frac{1}{2}$  of yeast, deducting the water which is foreign to it; that it produces a little more than 35 parts of carbonic acid; that nearly 58 parts of alcohol are obtained by the distillation of the vinous liquor, and that a little more than two parts of acetic acid, which was formed during the fermentation, and four parts of extract, remain. Without doubt these products will vary according to the differences of the saccharine substance, but they are sufficient to give an exact idea of fermentation.

At first Lavoisier was of opinion that the formation of alcohol was owing to the decomposition of the water; but the analysis which he made of the sugar showed him that the 0.64 of oxygen which it contains, were sufficient to explain the produc-

tion of the carbonic acid and that of the acetic acid which take place in the vinous fermentation. In fact, because it disengages carbon and oxygen, as is observed by Chaptal\*, the hydrogen remaining the same, "the characters of this element must predominate, and the fermentescible mass will attain a point at which it will offer only an inflammable fluid."

The extract left by the distillation of wine gives an acid, by distillation, analogous to the acetic acid, and which exhales ammoniacal vapours when it is saturated with lime: the acetic acid itself contains azote in its composition: the azote of the ferment, or at least a part of it, is therefore found in these products.

At first the ferment seems to act on the sugar by the disposition which one part of its carbon has to combine with oxygen. Thenard observed that yeast readily absorbed the oxygen with which it was kept in contact: it is the same with gluten, whose colour changes and soon grows darker.

When the vinous fermentation is completed, or approaches its end, some of the ferment still remains in solution; but then it exercises a different action, it produces another modification, which is to be examined; it causes the wine to become sour, particularly with a certain elevation of temperature; that also which was deposited contributes to this effect.

This ulterior action of the ferment explains the

\* *Elém. de Chim.* Tom. I.

necessity for attending to the clarification of wine which it is intended to preserve, for by it the ferment, whose prolonged action would have become injurious, is separated; it is probable that the utility of sulphuring consists in coagulating this soluble part of the ferment.

The preceding observations show that the knowledge acquired on fermentation, enables us to reduce the art of making wine to as exact principles as any other art whatever: they perhaps throw some light on the excellent precepts given by Chaptal\* on this subject.

There must be a certain proportion of ferment and saccharine matter in a given quantity of must; it is generally the latter whose proportion is too small: it may be augmented by the addition of sugar, or of any other saccharine substance. A part of the ferment may be separated, but probably this is deficient in wines which remain soft and flat; the scum, therefore, is not an useless recement; it contains a necessary ingredient, which, in some circumstances, it might be well to augment instead of diminishing it: the more the contact of this ingredient with the saccharine substance is promoted, the more activity it gives to the fermentation. This sediment must be carefully separated when the wine has arrived at the desired degree, but the separation must not be effected before this epocha. The action which it would exercise after it, would be injurious. It is

\* De l'Art de faire les Vins. Ann. de Chim. Tom. XXXVI.

still unknown in what the effects of the tartar consist, or even if it is produced in the fermentation, as, the acetic acid is formed. With respect to the malic acid, which is found in a certain quantity in some wines, is it also a product of fermentation, or did it exist in the juice of the grape? The proportion of the water may be diminished by evaporating the must.

Hitherto I have supposed that vinous liquors only owe the changes they experience to the saccharine substance which they contain: but whether this substance can have a sufficiently great difference of composition, or whether it can be divided in two parts, of which, one has properties analogous to those of starch, and the other, to those of sugar, the properties which suppose the existence of these two substances, or which are explained by it, are observed in most wines.

When the wine has arrived to a certain degree of the slow fermentation, it frequently becomes sour, and is changed into acetic acid: the elevation of the temperature and the contact of the air, whose oxygen is absorbed, favour this change. Nevertheless some saccharine or generous wines do not undergo this alteration, according to the observation of Chaptal; some others, on the contrary, experience it very readily. This difference seems to prove that some wines are produced from a must which contained only a saccharine substance, while that from which others are formed had also a substance much more disposed to acetification.

When

When the acetous fermentation takes place, the vinous liquor becomes turbid, and at length is clarified by a deposition which, in a great measure, is owing to a new separation of the ferment. It appears therefore that the ferment which remained in solution, produces the vinous fermentation while it meets with the saccharine substance, that when this is nearly exhausted, it exercises a weaker action, which usually requires a higher temperature, on another substance which is analogous to starch, and that then it produces acetic acid.

The oxygen which is absorbed during the acetic fermentation, according to the observation of Rosier, may serve for the decomposition of the vinous combination, by combining with the hydrogen, or else it enters immediately into the composition of the acetic acid; but to judge from the spoiling of wine left in contact with the air, it produces much more of the first effect than of the second. Nevertheless the production of acetic acid is not always owing to these two causes; it is formed during the vinous fermentation of sugar and yeast, even without communication with the air: it is true, it may then be owing to the portion of starch which the yeast always contains; this subject requires elucidation.

Parmentier, Deyeux, and Vauquelin, have examined the *sour water* of the starch makers, which contains the results of the fermentation of the farina left to itself and to the action of water; they obtained from it a little alcohol, a considerable quantity



quantity of acetic acid, and Vauquelin found a little ammonia and phosphate of lime in it\*.

It is natural to attribute the small quantity of alcohol to the minute portion of the saccharine substance which is contained in the farina: the ammonia and phosphate of lime are indubitably products of the putrefaction of a portion of gluten.

Vauquelin observes that, in the fabrication of starch, all that which existed before the operation is not extracted, and that a part of it must have been destroyed by the acetification: the gluten and the substance which produces the alcohol can only contribute a very small proportion of the quantity of acetic acid which is formed, either by putrefaction, or by the vinous fermentation.

I exposed a mixture of gluten and starch, both carefully washed, to a temperature a little raised, and with a certain quantity of water, acetic acid was quickly formed without any indication of a spirituous liquor; but the acid was soon saturated in part with ammonia, so that the gluten was not long in entering into putrefaction.

The preceding observations seem to me to prove that acetification is principally owing to the action of gluten, or of a substance which nearly resembles it, on the starch, or on an analogous substance, although it can take place in a slight

\* Ann. de Chim. Tom. XXXVIII.

degree in the vinous fermentation, or by the action of oxygen on the wine.

Panary fermentation has much similarity with the acetous; it is established between the gluten and starch when they are so combined as to be able to act on each other; I have ascertained that much carbonic acid is disengaged: yeast accelerates this fermentation, because it has less coherence than gluten; leaven produces the same effect, because the incipient fermentation which it has experienced has also diminished the cohesion of its particles, and disposed it to exercise<sup>1</sup> its action: hence it may be employed as a ferment to saccharine substances: the acidity which it has acquired may promote this effect, by occasioning a little less insolubility in the gluten. As the reciprocal action is weaker in this fermentation than in the vinous, it requires a more elevated degree of heat. When it is advanced, the gluten can no longer be separated from the starch, and it is afterwards blended with the acetous fermentation. Thus the cereal seeds may experience different changes according to the state of the gluten, and of the starch which they contain: if these two substances remain insulated, humidity causes the gluten to enter into putrefaction, and the seed loses the property of germinating<sup>1</sup>; if they are blended, the panary or acetous fermentation is established between them, particularly when their action is facilitated by that of a more attenuated gluten; but to enable the starch to undergo the  
vinous

vinous fermentation, it must abandon part of its carbon, and thus acquire the properties of a saccharine substance; hence the preparation of beer commences by germination. In the juices of the sweet fruits, the saccharine substance is already produced, they can therefore pass immediately to the vinous fermentation.

Chemists are divided as to the existence of alcohol in wine: some think it is ready formed; others only consider the wine as a substance disposed to produce it by the action of heat.

By dissolving the residuum of distillation in the liquor which has passed into the receiver, we are far from obtaining a liquor resembling the wine which had been the subject of the operation, and if the alcohol was ready formed, it could rise at a heat below what is necessary for the ebullition of water, since the term of its own ebullition is  $66^{\circ}$  of Reaumur's thermometer: it would only carry with it a quantity of water nearly corresponding to the tension of the latter. The acceleration of the term of ebullition, which I have supposed (244, 245) could only produce a small effect: alcohol would be obtained at once, with less heat, as it is obtained from wine with which alcohol or brandy has been mixed.

It appears to me, therefore, that alcohol has not, at first, an insulated existence in wine, although a little may be found in generous old wines, but that, laying aside the tartar and the other acids, this liquor must be considered as an  
uniform

uniform compound, in which, according to the opinion of Chaptal, the properties of hydrogen are predominant : heat disposes this elastic principle to separate, but its elasticity being balanced by the affinity which retains it in combination, a division of the elements takes place in the ratio of these two forces, and a liquid passes in distillation, in which the properties of the hydrogen have become much more predominant, while the other principles of greater fixity remain and form the extract : a second distillation of the spirituous liquor separates the water, which was only retained with the alcohol by a weak affinity.

Even when the extract is obtained from a liquor formed by means of sugar and yest, it retains acetic acid, as I have observed before, and it gives an acid product by distillation ; but if lime is added to this acid, which is of an acetic nature, ammoniacal vapours are disengaged : the acetic acid itself holds azote in its composition, as was shown by Proust\* ; whence it follows that the charcoal which remains in this operation will also conceal it, for the charcoal of substances containing azote can form Pruffic acid, and Proust has observed that it was contained in the residue of the distillation of acetate of pot-ash.

By the action of some acids, alcohol undergoes a change which produces new properties ; it passes to the state of ether.

\* Journ. de Phys. Tom. LVI.

Since the muriatic acid is incapable of producing ether, except when it is in some combinations in which it is supposed to be oxygenated, it has been thought that oxygen was necessary to the composition of the ether, and that the alcohol received it from an acid to pass into that state; this opinion has been strengthened by the supposition that acetic acid which is capable of producing ether, differs from the acetous acid by an excess of oxygen.

We are indebted to Fourcroy and Vauquelin for some very interesting observations on the action which sulphuric acid exercises both on vegetable and animal substances, and on alcohol\*, and also on the production of ether.

They observed that this acid separated a carbonaceous substance from it, that at the same time its concentration diminished, and that consequently it produced water: they explain the conversion of alcohol into ether by this action: the oxygen and the hydrogen of the alcohol are determined to form the water, and a part of its charcoal is separated, so that alcohol differs from ether, according to them, by containing more carbon and less oxygen and hydrogen, and the sweet oil which succeeds to its production, is to the ether, nearly what the alcohol is to it: they show that the production of the ether precedes the formation of sulphureous acid, and that conse-

\* Ann. de Chim. Tom. XXIII.



quently the sulphuric acid does not contribute to it by yielding oxygen.

I shall allow myself some observations on this luminous theory.

1st. It is not charcoal which is separated by the action of the sulphuric acid, but a resinous or bituminous substance, which, after being well washed, yields an acid and an oil by distillation.

2d. The production of an acid does not seem to me to be a constant effect; I did not perceive any by causing sulphuric acid to act on sugar. If this acid is concentrated, sulphureous acid is formed; if it is sufficiently diluted, only the separation of the black substance is perceived without any odour of acetic acid.

That which is observed in general in the action of a liquid on a substance whose composition is changeable, happens therefore here: the sulphuric acid tends to combine with every thing which can take the liquid state, thus it determines the formation of the water: on the other hand a solid substance is produced with proportions in which the element which has the greatest disposition to solidity, predominates: this phenomenon is similar to that of the separation of a soluble and an insoluble sulphate of mercury by water (387).

If, in this separation, there is an excess of oxygen in the soluble part, it can form a soluble acid; but its formation is not a necessary effect of the action of the sulphuric acid, since sugar treated with this acid did not, perceptibly, emit the odour  
which

which would have discovered the acetic acid even if a small quantity of it had been produced.

If we apply these considerations to the transformation of alcohol to ether, we shall see that there is a separation of a resinous substance, and a production of water ; but here there is a great excess of hydrogen ; what then becomes of it ? it will tend to separate, by its elasticity, which is increased by the heat, and to form an inverse combination to that of the substance which becomes solid, that is to say, a combination in which the hydrogen predominates : this is ether. Hence it follows that the ether will contain a much greater proportion of hydrogen than the alcohol, and much less oxygen : my colleagues, however, admit of a greater proportion of oxygen in it.

If alcohol is passed through a red-hot tube, carburated hydrogen gas is disengaged, of a great specific lightness, but an acid liquid is distilled, in which there is consequently an excess of oxygen : if ether is submitted to the same operation, carburated hydrogen is also disengaged, which has a greater specific gravity than the former, but the same quantities of carbon and hydrogen, in the same weight, as was observed by the Dutch chemists \*. This gas does not contain carbonic acid, and no liquid acid is formed, as in the destruction of alcohol.

When alcohol is decomposed by oxygenated muriatic acid, the residue is a substance somewhat

\* Journ. de Phys. An II.

resembling

resembling that obtained by it from sugar itself\* ; but ether seems to be entirely reduced to water, and to leave only a little thick oil †.

If there was a more considerable proportion of oxygen in the ether, it must be injurious to its greater inflammability, and, by the strong action which it exercises, to its specific lightness.

Although the last experiments were not made with that care which the exact comparison of alcohol and ether requires, they nevertheless concur with the indications of the theory to prove that ether contains a smaller proportion of oxygen than alcohol.

The formation of sweet oil is accompanied by the production of sulphureous acid, which shows that it contains a smaller proportion of hydrogen and a greater of oxygen, than ether.

Fourcroy and Vauquelin are of opinion that acetic acid is formed with the ether: Pelletier did not perceive any, nor did Pronst ‡. This result must therefore be considered as doubtful; but it is desirable that it should be ascertained, for the formation of acetic acid would prove that azote enters into alcohol: this should also be applied to the acid which is formed when alcohol is passed through a red-hot tube.

In the formation of nitric ether chemists know that acetic acid is produced, but the origin of the

\* Mém. de l'Acad. 1783.

† *Ibid.* Tom. II.

‡ Journ. de Phys. An II.

azote which enters into its composition is attributed to the nitric acid. In this operation a peculiar gas is produced, which was observed by Pelletier, and analyzed by the Dutch chemists: this gas is inflammable; it is soluble in water; it combines with the alkalis; it arises from the ether and the nitrous gas, which maintain a separate existence, but nevertheless form a combination whose properties are common until a superior affinity breaks it: this is a new example of an inflammable gas which contains a considerable proportion of oxygen. The disengagement of this gas should be avoided in the production of nitric ether, because it abstracts the ether.

The causes of the production of ether show why some acids are incapable of producing it: Pelletier was unable to obtain ether with the phosphoric and arsenic acids because they have too little action on water: acetic acid must be in the state in which it is known by the name of radical vinegar, because it is only in this state that it is sufficiently deprived of water: muriatic acid must be combined with a very oxidized metal, because then, deprived of water and very concentrated, it has a strong action on this liquid, as was shown by Adet, with the fuming muriate of tin (393).

In the distillation of vegetable substances, other separations take place, and other combinations are formed, determined by the composition of the substances which undergo this operation, by the temperature and the other circumstances which can

can modify chemical action : by a moderate heat, a volatile oil is changed into a more volatile oil and a resin ; the first, subjected to a higher temperature, is reduced into carburated hidrogen gas and carbonic acid ; a great part of the charcoal remains fixed. The resin gives the same products, by the same examination, but in different proportions ; the charcoal which it leaves is much more abundant.

The products also differ according to the composition of fat substances as well as their properties : the fixed oils seem to contain more oxygen and less carbon : with a greater proportion of oxygen they pass to the state of tallow and wax ; they yield more acid in their decomposition.

The substances which contain much oxygen give oxi-carburated hidrogen in their decomposition. The gazeous products vary, as was observed by Lavoisier, according to the quicker or slower action of heat, because, in the first case, water may be decomposed, and, in the second, it may pass in distillation before it experiences this decomposition.

The azote which is found in several vegetable substances enters into a more intimate composition with the hidrogen, and forms ammonia ; sometimes also Prussic acid. The charcoal retains part of the azote ; the earths and undecomposable salts remain blended with it.

All these changes are owing, 1st, to the affinity which tends to unite the different elements pre-



sent, or to separate them by the solidity, or the elasticity determined by the proportions in which their reciprocal action is most energetic, and by the temperature: 2d, to the reciprocal action of the compounds which tends to give them a common state of liquidity, or to separate the parts which differ by their disposition to the solid or elastic state.

If the applications of chemistry to the composition of vegetable substances, to their production and to their reciprocal action still present many undetermined objects; if the theory is limited to forming conjectures on many of these objects, which cannot be established but by a succession of inquiries; or if there is a certain number of them on which only hypothetical ideas can yet be obtained, how much greater must be the difficulties which offer to the knowledge of the properties of animal substances, in their relations with the elements which compose them, and with the successive changes which they experience!

A greater number of elements enter into the combinations which form animal substances: azote, which vegetable substances do not always contain, or have only in a small quantity, is a necessary part of those which are animal: sulphur and phosphorus seem to be found in all of them: they all contain considerable proportions of hydrogen: hence, unless they have acquired a consistence which can maintain them in their state, they are very unstable and very liable to experience

rience variations, and the more so because they receive but little oxygen into their composition, which by the force of its action might give more stability to it.

The difficulty of these applications is considerably increased when the attention is directed to the phenomena of the living animal: the respiration, which keeps the living body at an elevated temperature; the circulation, which unceasingly renews the contact of substances, different and of a variable nature, in vessels equally different and whose action is constantly modified by the vital properties, produce continual changes and new combinations.

When these difficulties are weighed, we cannot but be surprised at the precipitation with which some have been eager to give chemical explanations of all the phenomena of the living animal.

On the other hand, some celebrated physiologists are of opinion that the phenomena of the living body are entirely unconnected with the laws of physics, and are wholly owing to a vital force, which they employ vaguely in all their explanations; according to them, the blood itself, and the other liquids, are endowed with this force, which is predominant in all the changes which they experience; they might with the same reason say that animated substances have neither weight nor tendency to combination, and that the most powerful chemical agents lose all their energy on a substance which is governed by such a force.

Every thing dependent on the vital action, whose distinct effects may be perceived, such as those arising from the sensibility, the animal contractibility, the organic contractibility, should certainly be distinguished.

The observation of these effects, the knowledge of the organs which produce them, of their distribution, of their relations with each other, and of their peculiar affections, even the modifications which may result from them in the reciprocal action of the liquids and solids, are the subjects of a series of inquiries which must not be confounded with those whose object is the other physical phenomena; but it must not thence be concluded that the physical causes which exercise their action on brute substances, are not to be taken into physiological considerations. Does not the light act upon the eye conformably with its properties? Do not the vibrations of the air communicate impressions to the ear which correspond with their variations? Do not nitric acid and pot-ash dissolve a living substance, as though it was deprived of life? Are not the phosphate of lime of the bones, the phosphoric acid, and the phosphates of the urine, combinations whose elements have been subjected to affinity, independently of vitality?

It appears to me, therefore, that the combinations which take place in the living animal, are equally the effect of an affinity which is varied by the circumstances, as in the other chemical phenomena, but these circumstances are very multifarious;

farious ; the organic action may also cause them to vary by the contraction and motion occasioned by the organic sympathy and the vital affections.

The chemical dispositions which may be found in animal substances depend on the elements which compose them, on their proportions, on their state of combination, and particularly on their softness and their solidity ; thus, all other things being equal, a greater proportion of azote will render them more putrescible. It is obvious, therefore, that to ascend to the source of the chemical properties of the different animal substances, we must begin by making an exact analysis, and determining the proportions of their elements. Fourcroy is almost the only one who has engaged in this subject with any method ; but it is a work which can be brought to the requisite precision only by long and multiplied researches, and, until lately, chemistry did not possess the necessary ground-work.

Vitality belongs only to substances which have a certain proportion of azote and of hidrogen : it may be said that a moderate action of these elements is necessary for the establishment of another order of properties, and that these properties are modified according to the chemical qualities of the combination ; thus the sensibility is exquisite, with a softness allied to the degree of solidity necessary to the communication of the vital action, which requires an intercourse between the integrant particles of a substance ; such is the nervous  
pulp :

pulp : as soon as the solidity is augmented to a certain degree, the sensibility diminishes and even disappears ; if the solid particles resume their softness, it frequently happens that they acquire a new sensibility.

The progress of life is particularly seen in microscopic animals ; rudiments which offer only the appearances of vegetation, and which also retain them in one part of their growth, are changed into animals : thus the green matter which Priestley took for a common vegetable, is, in great part, composed of animalculæ, which can afterwards be multiplied in different manners, as was observed by Ingenhouz\*, and give oxygen gas by exposure to the light.

The fuci, the byssi, the tremellæ, and an indefinite number of other substances, which enjoy the properties of polypit, offer phenomena common to the vegetable and animal state, and pass from one to the other.

Some of these substances may arise from the decomposition of animal substances, which, if their quantity is small, compared with the water, do not, in this case, putrefy ; but if they experience a commencement of putrefaction, the products, particularly the odour, which is an indication of it, disappear, and oxygen gas is disengaged.

\* Nouv. expér. et observ. Tom. I.

† Recherch. chim. et microscop. sur les conferves, les bisses, tremelles, etc. par Girod Chantrans.



This remarkable effect, observed by Priestley\*, does not take place without the assistance of light: in the dark, only the products of putrefaction are obtained.

The production of these substances, which have a vegeto-animal organization, seems always to require the concurrence of light; it is always accompanied by a disengagement of oxygen gas; it requires, therefore, a decomposition of water, whose hydrogen, consequently, enters into their composition.

Azote also enters into them, for they putrefy readily, and Girod Chantrans obtained ammonia by their analysis. It appears that the animal substances furnish this azote, which renders them particularly proper for their ready production: they may, however, be produced or grow without the concurrence of animal substances, and then they appear to take the azote which is dissolved in the water: hence it arises that, according to the observation of Spallanzani†, microscopic animals die soon, when the water they inhabit is not in contact with a certain quantity of air. Some vegeto-animal substances may receive a considerable increase in pure water, by means of some fragments put into it, as was shown by Girod Chantrans, for the purpose of ascertaining their composition; do these substances then contain the

\* Expér. et observ. sur diff. branches de la Phys. Tom. III.

† Oeuvres. Tom. II.

great proportion of calcareous earth which he found in them? It remains to be examined whether these green productions can arise from the decomposition of carbonic acid, when they are not owing to an animal substance. It is probable that they retain a little oxygen in their composition, since oil is obtained from them by distillation.

We are already indebted to Cabanis for several important considerations on the passage of the brute substance to the animated substance; he will furnish new information on this subject, since he has announced that he continues to be occupied with it\*.

Some fishes seem to grow by a similar process: Rondelet has observed that some of them acquired a considerable weight by living in pure water. It is probable that the decomposition of water takes place abundantly in all animals, for they become very fat by living on aliments which contain but little hydrogen; and, in general, all animal substances have a great proportion of hydrogen.

The azote accumulated in animals which respire arises partly from the respiration itself. Priestley had observed that a considerable absorption of this gas took place, but there might have been some cause of uncertainty in the process which he employed: Davy, who conducts his experiments with great accuracy, has removed every possible doubt; he observed that in the ordinary respira-

\* *Rapports du physique et du moral de l'homme. Tom. II.*

tion, the quantity of azote gas absorbed is nearly a sixth of that of the oxygen gas, and that only a part of the latter is employed to form the carbonic acid, so that another part serves for the composition of water, or enters into some other combination\*.

The chemical action of substances which enjoy life being brisker than that of those in vegetation, combinations much more difficult to form will result from it. Lime and phosphorus are perhaps of the number of these productions, for the experiments of Vauquelin, which it would be important to repeat and vary, indicate a quantity of lime and phosphoric acid in the excrements of a fowl, much greater than what existed in the food with which it was nourished†. It is to be wished that Girod Chantrans had also examined whether the animal plants produced phosphorus or phosphoric acid.

Animal substances, abandoned to themselves, enter into putrefaction; the changes which they undergo from it; the term at which their decomposition is stopped according to the circumstances; the combinations which are formed, are still far from being known, as has been observed by Proust.

If putrefaction is established with but little water, a great quantity of inflammable gas is dis-

\* Philos. Trans. 1790.

† Bibl. Brit. Tom. XXI.

engaged, which is carburated or oxi-carburated, and which is mixed with a certain quantity of carbonic acid: if the gas is washed, the carbonic acid separates, and it loses much of its stench; when its disengagement is obstructed by stopping the flask, the putrefaction soon ceases, and does not resume its progress until the gas, which produces a compression, is permitted to escape: if there is much water with the animal substance, only a small quantity of gas is disengaged, but the liquid becomes very fetid: finally, if the proportion of water is very considerable, and if the vessel is exposed to the sun, there is no putrefaction, but a production of animated matter, and a disengagement of oxygen gas. When the substance which putrefies is in contact with a great quantity of air, carbonic acid is produced, but not the inflammable gas, and the volume of the elastic fluid diminishes instead of augmenting; the substance which then undergoes putrefaction, loses its consistence and becomes viscous and almost liquid, so that there is unquestionably a production of water; at the same time ammonia is formed, and, at the beginning, an acid whose traces disappear by the augmentation of the ammonia; when the air has been successively renewed, the putrid odour ceases to be perceptible.

The cause of the deadly influence of putrid emanations has not yet been elucidated: Priestley and Cavendish found that air might be rendered infectious without its deleterious qualities being discoverable

discoverable by eudiometric tests. By combining the very small number of observations which have been made on this subject, it appears that the product which yields the putrid odour has but little gaseous disposition, and that the quantity dissolved by the gases which are in contact with it, or which are disengaged during putrefaction, is scarcely appreciable. Crawford observed that it did not take the gaseous state by distillation\*. The precipitates which have been obtained from some metallic solutions by the ichorous sanies, may be attributed to a little sulphurated hydrogen. This combination must necessarily have azote, since substances without azote do not putrefy, and probably those are most putrescible which contain the greatest quantity of it. Whatever this substance may be, chemistry has been able to destroy its deleterious effects, even without being acquainted with it; for this service we are indebted to Guyton, and its importance will become greater as it is better known †.

The acids may be serviceable in removing infection, either because they destroy the putrid combination, as is very probably done by the oxygenated muriatic acid, and perhaps by the nitric and sulphureous acids, or by simply com-

\* Philos. Trans. 1790.

† Traité des Moyens de désinfecter l'Air.



bining with the putrid substance. It is thus that the muriatic acid appears to act; but it must not be concluded from this, that the substance is an alkali, for the alkalis have also the property of combining with it, and, at least, lessening its effects; antiseptics prevent them by producing a combination with animal substances, which offers more resistance to the causes of decomposition.

The distinctive power of opposing all putrefaction, alone, is attributed to the vital action; but the ferment of an animal nature does not enter into putrefaction in the vinous fermentation, or even in the acetous; several antiseptic substances prevent its appearance by their combination; the gluten of flour does not putrefy without a certain degree of humidity, and putrefaction goes on in some substances which are not wholly deprived of the vital influence. It appears to me, therefore, that the chemical causes which are opposed to putrefaction during life, may be sought for and found in the succession of combinations which are effected, and in the continual evacuation of the urée, which contains much azote, according to the excellent observation of Fourcroy\*, whether the azote enters into the composition of the urée, as he believes or is previously found in it in the state of ammonia, as is announced

\* Syst. de Conn. Chim. Tom. X.

by Proust; the other excrementitious substances will also contribute to this effect; finally, the vital action will contribute to it by the motions and contractions which it produces, and which repel the objects which affect the senses in a certain manner.

Such of the animal substances as contain the least azote undergo only a commencement of putrefaction, and are changed into cheese; the properties of the caseous substance of milk appear to me to be owing to this circumstance: Hilaire Rouelle observed, that the gluten also experienced this change: on leaving the albumen of egg, coagulated by heat, exposed to the air, I observed that it passed slowly to the state of cheese. Vauquelin observed that acetic acid and ammonia were produced in the formation of cheese: this production seems to take place in all putrefaction.

The elements of animal substances separate at an elevated temperature, and form combinations determined by the volatility and the fixity: the azote and the hydrogen produce ammonia and Prussic acid; a great part of the hydrogen enters into the composition of carburated hydrogen and the oils; carbonic acid is also formed, either by the decomposition of water, or by means of the oxygen which entered into the composition of the animal substance; it is probably to the latter that an acid, analogous to the acetic acid, which

is

is found in the products of the distillation, is indebted for its formation; finally, the carbonaceous residue contains the phosphates and the different earths and oxides.

Indications of sulphur are also perceived in this operation: the charcoal retains azote and sulphur, by means of which it can form Prussic acid and sulphurated hidrogen.

CONCLUSION

## CONCLUSION

OF THE

## SECOND PART.



THE reciprocal affinity of all substances, and the dispositions belonging to them, and which depend on the relations between caloric and the particles which compose them, form the power which produces all the changes of combination which succeed each other in nature, and the phenomena derived from them: hence arise all the forces which are balanced, blended, or opposed; which are neutralized, or developed in their primitive energy.

In the first part of this Essay I have compared the effects of these general causes, to discover the laws which they follow; I have analyzed those of each disposition common to different substances. From these considerations I have concluded, that all the reciprocal action of bodies which tends to change their state of combination, is obedient to the same laws, and that all the phenomena which result from it are not the products

ducts of the affinity of the substances alone, but that they also depend on the dispositions which distinguish them, and on the changes which they experience from the circumstances in which they are found.

In the second part I have examined the particular dispositions of substances, and have endeavoured to discover the influence of these dispositions, and the modifications which they may produce in the exercise of the affinity peculiar to them, or which they may receive, in the effects of their action.

The individual qualities are connected by the tendencies to combination, which is their principle; it is by these connexions that the substances should be classed, and the chemical properties which distinguish them compared. Resting on these considerations, I have successively compared the substances whose energetic action produces the most distinct effects, contributes most to the phenomena, and becomes an instrument in the hands of a chemist.

If the chemical properties of the different substances are owing to their affinity and to their peculiar dispositions, those of the combinations which they form depend on the respective saturation, on the changes of constitution arising from the reciprocal action, and on the degree of force which maintains the combination: thus the properties of simple substances are not only the cause of combinations, but also of their peculiar affections.



affections. I have endeavoured to follow them in the transmutations which they experience, and in the revivification which they owe to opposite conditions.

After having recognized the properties and substances which exercise a chemical action, we can proceed to the examination of the phenomena which are the consequence of it, but which often depend on a very complicated action, all the elements of which it is necessary to endeavour to distinguish.

In this examination, sometimes only results can be obtained which are capable of a double explanation; the causes of the phenomena may also be too complex to be distinguishable by actual data, and the combinations too unstable to ascertain the parts which compose them, or at least the state in which they exist.

When observation cannot attain to determinate results, it still remains in the power of chemistry to ascertain and unite the circumstances which can occasion a production or a phenomenon; thus it can be extended to the most obscure processes and the most complicated phenomena of the arts, so that the applications of chemistry have no other limits but those of the reciprocal action of bodies.

In inquiries whose object is the general properties, as well as in those employed on the peculiar properties and the applications of chemistry, whether a substance or a phenomenon is analyzed,

we must only decide from accurate experiments, all the circumstances of which have been examined with care, so that this precision in the art of experiments should be the constant solicitude of chemists; but it would be a gross error to endeavour to collect the results of insulated experiments without being guided by an enlightened theory. Is not this theory the fruit of experiments directed to the more or less precise determination of the general properties? Each principle which it establishes will be a consequence of experiments made on a common property, and without these principles we shall only obtain facts incompletely observed, unconnected with each other, and uselessly accumulated.

I have endeavoured to estimate all the forces which contribute to chemical action, and afterwards the principal properties of the substances which exercise these forces: I have examined the causes, and have endeavoured to balance them with their effects; but, in concluding this Essay, I repeat that I am persuaded that, both in the discussion of principles, and in the numerous applications which have offered, it has frequently happened that I have relied on facts whose accuracy was not sufficiently confirmed; that I have attributed effects to a cause of which they were independent, and have given too much authority to views which, as yet, are only conjectural: still I shall have accomplished my object, if I engage the attention of chemists to principles which

which have been admitted with too much confidence, and to properties which it appears to me important to establish with more care, that the science may gain strength in its rapid progress: I shall be the most vigilant among them to discover the causes of error which may have imposed upon me.

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# NOTES

## TO THE

### SECOND VOLUME.

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#### NOTE XIX.

PRIESTLEY describes \* several experiments which he made on the reduction of oxide of iron, exposed to the focus of a burning-glass in a vessel filled with hydrogen gas. From these experiments Kirwan drew an objection to the antiphlogistic theory: Foureroy, in whose opinion I partecipate, replied †, “ that the hidrogen takes only  
“ that quantity of the oxigen from the oxides of iron,  
“ which they contain beyond the term of their black  
“ oxidation, because this quantity has more affinity with  
“ the hidrogen than with the iron; but when the reduc-  
“ tion has reached this point, it stops: the latter portion  
“ of oxigen combined with the iron is so much more  
“ adherent to it, that it does not tend to unite with the  
“ hidrogen.”

These observations, which are very just as to the term of the action of iron on water, suppose that Priestley had

\* Exper. and Obs. on diff. Branches of Phys. Vol. IV. Sect. III.

† Essai sur le Phlogist. p. 252.



submitted iron very much oxidized to the experiment, and that the iron was only brought to the state of black oxide: but, 1st, the iron, oxidized at the commencement by combustion in oxygen gas, had only acquired an augmentation of about one-third of its weight, according to Priestley's observation; it was similar to the black scoriæ of forges, and therefore differed but little, in its state of oxidation, from what we call *black oxide*, such as it is obtained from the decomposition of water: 2d, Priestley says positively, that, after the action of the hydrogen gas, the oxide had become *perfect iron*: now he could not have been deceived in this respect if the metal had only passed from a state of greater oxidation to that of black oxide, and the detail of his experiments show clearly, that if the reduction was not perfectly complete, it was at least much farther advanced than we have supposed it; so that the result of this action of hydrogen must not be confounded with that arising from the decomposition of water.

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#### NOTE XX.

IN my observations on charcoal and the carbonated hydrogen gases\*, I employed the production of an inflammable gas, obtained by passing the electric spark into carbonic acid, as was done by Priestley and Van Marum: I adopted Monge's explanation without restric-

\* Mém. de l'Institut. Tom. IV.

tion, attributing this production wholly to the decomposition of the water; so that, with him, I took this inflammable gas for hydrogen gas, and I concluded that the diminution of volume experienced by the carbonic acid was owing to the privation of water.

I ought to have considered, that, in this case, the carbonic acid must have experienced the same effect as when it is exposed to a high temperature in contact with a metal capable of oxigenation; but I suffered myself to be imposed upon by the quantity of oxygen which this gas seemed to absorb in its combustion, and which corresponded to that consumed by hydrogen gas, which is much more considerable than is required for oxi-carburated hydrogen.

Theodore de Saussure has examined the results of the action of the electric spark on carbonic acid \* with more care; he has shown that the inflammable gas obtained is of the same species as that which is called carbonous gas, and that the carbonic acid which resisted the decomposition did not dilate when brought into contact with water; but, in my opinion, the conclusions should stop here.

The results of this experiment are among those which are capable of a double explanation, and which, for that reason, are not calculated to elucidate the object under discussion.

Nevertheless, analogous facts prove that the electric spark has the property of decomposing water, whose oxygen and hydrogen can then enter into other combinations.

Austin exposed † the gas obtained from the distillation of acetate of pot-ash to the action of the electric

\* Journ. de Phys. Tom. LIV.

† Philos. Trans. 1790.

spark ; this is a carburated hydrogen gas, or at least there can be no doubt that it resembles it greatly, judging by the great proportion of oxygen which it requires for its combustion ; he observed that, by this operation, the gas acquired a volume more than double what it had at first, and he was of opinion that it afterwards required a greater quantity of oxygen, and, nevertheless, that it gave less carbonic acid ; whence he concluded that the charcoal was decomposed by the action of the electric fluid.

Henry has confirmed the great dilatation, but he has shown, by much more accurate experiments \*, 1st, that the quantity of carbonic acid which can be obtained by the combustion of the dilated gas, is precisely the same as that given by a corresponding quantity of the primitive gas, and he has removed all suspicion of a decomposition of charcoal : 2d, that the dilated gas requires nearly a fourth more of oxygen for its combustion, so that hydrogen gas is evidently disengaged, which can only arise from the decomposition of the water : 3d, that this decomposition is not occasioned, in this instance, by the oxidation of a metal, for he was able to produce it when he retained the gas by means of gold ; but he shows that it is accompanied by the production of a little carbonic acid.

He observed that the gas which had been submitted to the action of an alkali for several days to carry off all the hygrometric water, only experienced a dilatation equal to one-sixth of what it would have been without the action of the alkali ; but that by adding a little water it became similar.

These experiments prove incontestibly that the inflammable gases, which contain charcoal, may experience a decomposition of water, and that that which may be car-

\* Philos. Trans. 1791.

ried off by eudiometric means is not the whole quantity which can contribute to this phenomenon.

It must be observed, that the hygrometric water which a gas can contain at 15 degrees of the thermometer would scarcely exceed a milligramme in 100 cubic centimeters, which would only yield about the 50th of the volume of a gas of hydrogen gas; and that hydrogen gas, azote gas, and oxygen gas, submitted separately to electricity, do not sensibly yield hydrogen gas, although they contain hygrometric water.

The gases which contain carbon are not the only ones in which the decomposition of water can be proved. Henry having subjected muriatic gas to the electric spark, obtained an inflammable gas from it, without the acid having suffered any decomposition\*; in this case, no other cause of the production of hydrogen gas can be imagined, except the decomposition of water, and no other species of inflammable gas but that which arises from it immediately, that is to say, hydrogen gas, can be suspected.

Henry also employed the most powerful eudiometric means to deprive the muriatic gas of all humidity; nevertheless, 100 measures gave 6 of hydrogen gas, that is to say, at least three times as much as if the gas had been saturated with hygrometric water, and supposing that there was only this water capable of being decomposed: it must be remarked, that the gas which had not been subjected to desiccation did not yield .01 more of hydrogen gas.

During the disengagement of the hydrogen gas, muriate of mercury was formed, so that the two constituent parts of the water were equally manifested by this decomposition. Fluoric gas offered the same phenomena.

\* Philos. Trans. 1800.

It is therefore ascertained that gaseous substances may conceal a quantity of water, which is not that which produces hygrometric phenomena (173): this combined water may be afterwards decomposed by the methods which favour another combination of its elements; but it is probable that the affinity retains a greater or less quantity of it, according to the nature of the gas, the force of the electricity, and the energy of the substance with which the oxygen tends to combine, and that then only a part of the combined water experiences a decomposition.

This combination of non-hygrometric water cannot be matter of surprise to Saussure, who has proved so clearly that alumine can retain a tenth of its weight of it, at a heat which melts iron.

If the great augmentation of volume experienced by the carburated hydrogen gas in the experiments of Austin and of Henry, is compared with the slight dilatation which carbonic acid undergoes when it is decomposed, and passes to the state of oxi-carburated hydrogen, it will be evident that two species of production of this gas by the electric spark must be distinguished, in the same manner as when it owes its origin to carbonic acid placed in contact with charcoal or an oxygenable metal (287) at a high temperature.

In the first case, the combined water is decomposed, and its two elements concur in the formation of the gaseous substance, whence it arises that the volume is more than doubled: in the second, the oxygen of the water and part of that of the carbonic acid are fixed in the metal, and then the transformation of the carbonic acid is made with an augmentation of volume scarcely perceptible: the effect of the condensation of the oxygen in the metal nearly counterbalances that of the dilatation arising from the hydrogen.

Saussure



Saussure has collected other interesting experiments in his Memoir ; he shows that when a mixture of hydrogen gas and carbonic acid is submitted to electricity, water and the gas which I call oxi-carburated hydrogen, are formed ; Clement and Desormes had produced a similar decomposition by passing hydrogen gas and carbonic acid through a red-hot tube ; Saussure observed, that when hydrogen was kept long in contact with carbonic acid gas, a similar decomposition was very slowly produced, accompanied by the formation of oxi-carburated hydrogen gas, so that heat and electricity only accelerate this effect.

These products of the slow action of gaseous substances have a remarkable similarity with those of the slow fermentations established by means of the reciprocal action of substances held in solution in a liquid (14).

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### NOTE XXI.

THE detonations which can be produced have relations with each other, and with the inflammation of combustible substances, which are worthy of examination.

Those which are produced with facility take place, either by an elevation of temperature, by compression, or by percussion ; they are the effect of a combination which is produced, but since the necessary compression cannot excite a degree of heat near to that which must be employed to cause the detonation, the effects which are produced must not be attributed to the action of heat alone : the approximation of the particles, which are near the term at which they can combine, augments the action

action of their affinity, it therefore favours their combination: at the same time the caloric, whose disengagement is occasioned by this approximation, is favourable to the production of the gaseous substances which may be formed, and, in part, passes in combination with them: the excess resulting from the combinations formed by this double action, raises the temperature, and tends to dilate the gaseous substances proportionally: hence the effects of the detonation. I have explained (177) how heat, communicated to one gas, can, by the compression which it causes, produce its combination with another gas; but I purpose to inquire here what are the differences between inflammation, and detonation or fulmination, and what the dispositions and the circumstances are which determine one rather than the other. These dispositions must be considered, both in the oxygen, which is the ordinary source of the disengaged caloric, and in the inflammable bodies.

The oxygen may be condensed, and, nevertheless, retain a great part of its caloric; it is in this state in the nitrates, in the super-oxygenated muriates, in the oxides of gold, silver, and mercury, and, perhaps, in that of platina: these, therefore, are substances which can furnish oxygen in the state most suitable for detonations.

Van Mons says \*, “ the oxides of gold, silver, and mercury are found to hold the first rank among the fulminating substances: the oxygenated muriate of pot-ash does not yield effects as uniform as those of these oxides.”

If, however, a nitrate has an oxide of these metals for a base, the tendency of the oxygen of the nitric acid to combine with an inflammable substance, seconded by that of the oxygen in the metallic oxide, may render it

\* Ann. de Chim. Tom. XXVII.

very fit for detonations : thus Brugnatelli and Van Mons produced them by compressing these nitrates with phosphorus and sulphur, but particularly with phosphorus : the other nitrates with metallic bases have also produced this effect, which cannot be surprising, since nitrate of pot-ash has also this property.

The inflammable substances are the best adapted for detonations, because they have a greater disposition on the one hand, to combine with oxygen, and, on the other, to produce an elastic substance ; thus, the hidrogen being greatly condensed, and, nevertheless, retained by a weak affinity, in the ammonia, the great action which it exercises on oxygen will dispose it to produce detonations, by forming water which expands by means of the heat eliminated principally from the oxygen : charcoal is less calculated for this effect, because it inflames with more difficulty, and because less caloric is disengaged in the formation of carbonic acid : sulphur, which inflames more readily, which disengages much more caloric, and forms sulphuric acid, which, at a high temperature, is reduced into vapours, will produce detonations with greater facility than charcoal, and they would be more violent, if the acid was not frequently fixed with its base : finally, phosphorus, which is much more combustible, will detonate with much more facility, as was proved by Brugnatelli and Van Mons : but there is an observation to be made with respect to phosphorus, because the combinations it forms have a fixity which prevents them from taking the gaseous state without much difficulty. Van Mons has very judiciously remarked that part of the mixture with the phosphorus must escape the combustion to produce the requisite effect by its dilatation. He says “ whenever I struck these mixtures with a heated hammer, I always obtained a weaker detonation and a “ stronger inflammation, and when the hammer was too “ much

“ much heated, neither detonation nor noise was produced.  
 “ This is what I had observed before with the oxygenated  
 “ muriate of pot-ash, and seems to me to explain the  
 “ manner in which the phenomena of detonation are ef-  
 “ fected. A blow in the cold, by strongly compressing  
 “ the substance, and, perhaps, by exciting some heat,  
 “ effects the semi-combustion of the phosphorus, and,  
 “ consequently, occasions only the partial employment  
 “ of the oxygen, of which the portion not fixed in the  
 “ combustibile produces the noise by taking the elastic  
 “ state: at a more elevated temperature the phenomena do  
 “ not take place in the same manner, the whole of the  
 “ oxygen is consumed at once to burn the combustibile,  
 “ and hence the stronger inflammation and want of de-  
 “ tonation”.

Without excluding the action of the oxygen, part of  
 which is probably disengaged by the effect of the great  
 heat which is suddenly excited, without entering into  
 combination, it appears to me that the greatest part of the  
 effect must be attributed to the dilatation experienced by  
 the phosphorus itself, since, as Van Mons observes, par-  
 ticles of phosphorus which have not experienced combus-  
 tion always escape in the percussion, and he warns us to  
 be guarded against them: he also experienced that phos-  
 phorus alone could detonate by being subjected to a strong  
 percussion, but if all the phosphorus enters into combi-  
 nation with all the oxygen, there is, conformably to his  
 observation, a much more vivid inflammation and no de-  
 tonation, which is a proof that the latter requires the  
 sudden production of a substance which takes the elastic  
 state, agreeably to what I have asserted.

If the detonations produced by a blow, on which Four-  
 croy and Vauquelin have made some ingenious observa-  
 tions \*, are examined, it will be obvious that among the

\* Mém. de l'Institut.

metals, it is those which have a disposition to volatilize, and consequently to be reduced to gas, which produce the detonations with the super-oxygenated muriate of potash ; they are zinc, antimony and arsenic : the sulphuret of iron has also this property, but it owes it to the great proportion of sulphur which it contains. These chemists remark that the mixture of sulphur and charcoal detonates more strongly than sulphur alone, which must be on account of the carbonic acid which the charcoal can form ; but the sulphur facilitates and commences the effect, as in gunpowder (314) : they observe that of these mixtures, those which are the most readily inflammable produce a brisk flame, but without detonation, by being thrown into sulphuric acid ; they very judiciously explain the differences of this effect by the combustion, which, being made without resistance, is unaccompanied by the effort produced by the disengagement of a gas in percussion.

Compared with inflammation all the detonations are therefore an effect analogous to that which is produced by the simple combustion of hydrogen gas, when it burns quietly with the oxygen gas which is in contact with it, or when the mixture, previously made, detonates, by instantly forming the vapour of water raised to a high temperature, whence arises a brisk and sudden percussion : in the common combustion of charcoal the effect is successive, and the carbonic acid which is produced is not raised to so high a temperature.

To produce detonations by percussion or by an elevation of temperature, it is therefore necessary that there be oxygen condensed, but retaining its caloric, and an inflammable substance in combination : the conditions which promote this effect are, 1st, the weak adherence of the oxygen to the base in which it is condensed ; 2d, the strong tendency of the inflammable substance to combine with oxygen ; 3d, the great quantity of caloric which is excluded



excluded by the combination; and 4th, the volatility of the combination.

The rapidity of the explosion also contributes greatly to the effects of the detonation, and explains the differences found between them: a great rapidity in the effect of a small quantity of the produced gas causes the rupture of vessels which would have resisted the slower disengagement of a more considerable quantity of the elastic fluid, and, nevertheless, this detonation does not produce a very loud report, as is observed by Howard\*: a fulminating powder capable of shattering the vessels which confine it, would have only a very slight effect if its gas met with but little resistance to its expansion: I was able to decompose seven grains of fulminating gold in a glass retort, which, enclosed in a very strong metallic tube, but much smaller, would have broken it to pieces†. An observation of Howard shows very clearly that this rapidity of action is a much more powerful cause of the effects produced in a contracted space, than the elevation of temperature which augments the dilatation of the gas; he detonated a mixture of the fulminating mercurial powder, which he covered with gunpowder, but the latter did not detonate.

It is this rapidity of action which constitutes the principal difference between the powder made with the super-oxygenated muriate of pot-ash and the common powder, for the quantity of gas disengaged in the detonation of the latter must be more considerable, considering the azote gas; but the effect is much more rapid with the first, in which the oxygen passes more readily into combination; for this reason it bursts fire-arms more readily, it detonates by a much slighter percussion than is required for

\* Bibl. Brit. Tom. XVI.

† Mém. de l'Acad. 1785.

the common powder, and by these properties, it approximates to fulminating gold, silver, and mercury.

Thus the tranquil effects of the simple oxigenation, which sometimes has no other indications but those arising from the properties of the combinations which are formed, are connected, by an uninterrupted gradation, with the most splendid phenomena: if the same forces which produce it have a greater intensity, or if their energy is assisted by the circumstances, oxigenation gives place to combustion, and this to detonation; the mechanical effects of the latter are owing to the tension of the combinations which form, and which is increased by all the action of the caloric set at liberty.

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### NOTE XXII.

*Observations on the precipitates of metallic solutions, presented and read to the Institute on the 23d Ventose, in the year XI.*

The examination of several precipitates, formed in metallic solutions by the alkalis, proves that they retain some of the acid, and sometimes of the precipitant employed; this has caused them to be classed among salts with a *minimum* of acid, according to the denomination of Rouelle. This exact appreciation of the nature of precipitates was confined to a small number of those which had been analyzed, and the products of the precipitations continued nevertheless to be considered as pure oxides until the author of *Researches into the Laws of Chemical Affinity*, by applying his principles of chemical action to

the separation effected by the alkalis in metallic solutions, determined the true nature of these precipitates. In the memoir which I have the honour to present to the Institute, I purpose to add some new developments to this application of the theory, by extending the observations hitherto made to a greater number of metals: but before offering mine, I shall state concisely those which have been previously made on this subject.

Rouelle\* had discovered that several metals were capable of forming combinations with the acids, containing different quantities of the latter: among others, he instances mercury, which forms two salts with sulphuric acid, the one with an excess of acid and soluble, the other insoluble, which was designated by the name of turbith, and before his time had been taken for a mercurial oxide; antimony, the muriate of which, by affusion with water, gives a precipitate in which muriatic acid is found; bismuth, which by treatment with nitric acid, is similar to the antimony of the preceding experiment. These and several other analogous facts, determined this chemist to divide the saline compounds into salts with a *maximum* and salts with a *minimum* of acid. The objections of Baumé† to this doctrine did not prevent chemists from adopting it. Bayen supported it‡ by interesting experiments on the precipitates of the solutions of mercury, the principal results of which are, 1st, that the turbith is a salt with a *minimum* of acid, extremely little soluble; 2d, that pot-ash and soda precipitate a salt similar to the turbith from the acid sulphate of mercury, that is to say, a sulphate with a *minimum* of acid; 3d, that the precipitates formed in the corrosive muriate of mercury by the fixed alkalis, are muriates of mercury with a *minimum* of

\* Mém. de l' Acad. 1754.

† Chim. exper. et raison. Tom. II.

‡ Journ. de Phys. 1774, 1775.

acid ; 4th, that nitrate of mercury also gives salts with a *minimum* of acid ; 5th, that the precipitates obtained from the nitrates and corrosive muriates of mercury, by ammonia and lime, retain the acid and precipitant at the same time, so that they then form nitrates or muriates of mercury and lime, or ammonia.

To the knowledge of these insoluble combinations of mercury, Fourcroy has added that of the ammoniaco-mercurial sulphate, the mercurio-ammoniacal sulphate, and the soluble ammoniaco-mercurial muriate, which he has distinguished from the mercurio-ammoniacal muriate observed by Bayen : the memoirs\* in which these salts are described, contain a great number of experiments on the combinations of sulphuric acid with mercury, on the precipitation of this metal from its solutions in the sulphuric, nitric, and muriatic acids, as well as on the triple salts which it is capable of forming with each of these three acids and ammonia. They have all given a new degree of certainty to the results obtained by Rouelle and Bayen on this subject, and have greatly extended our knowledge of the mercurial compounds, the more so because he has admitted into his considerations that of the state of the oxidation of metal, which has great influence on the results. Several facts, however, do not appear to me to be in perfect accord with the theory developed by Fourcroy. Whatever mistrust an opinion contrary to that of so skilful a chemist may impress me with, I must indulge myself with some observations, in the hope that whether I have misunderstood his theory or have observed it inaccurately, they will induce him to point out my error.

On treating one part of mercury with half a part of concentrated sulphuric acid and stopping the operation at the

\*Mém. de l'Acad. 1790. Ann. de Chim. Tom. X. et XIV. Syst. de Conn. Chim. Tom. V. p. 510. et suiv.

moment at which there is no more mercury in the metallic state, a mass is obtained from which are separated by washing, first an acid salt, and afterwards a neutral salt; a sulphate with an excess of yellow oxide remains, on which water has no further sensible action: it appears to me that Fourcroy believed that mercury is at the same degree of oxidation in the neutral and in the acid sulphate; that in both it is in a very inferior state to that in which it is in the sulphate with excess of oxide; finally, that this last salt is developed in the sulphuric mercurial mass\*, obtained by the action of the sulphuric acid on mercury, only by a new absorption of oxygen, which he believed to arise from what is in solution in the water, or from the atmospheric air.

The property possessed by the muriatic acid of forming a soluble salt with a greatly oxidized oxide of mercury and an insoluble salt with a weakly oxidized oxide of mercury, renders it very proper to show with certainty the degree of oxidation of this metal in its different combinations. I shall employ this mode of proof to appreciate the oxidation of the different sulphates of mercury, such as they are described by Fourcroy: I shall afterwards detail the experiments which prove that the three sulphates may exist at different degrees of oxidation, and that, consequently, the property of being in this or that state of oxidation cannot be attributed to them as a distinctive character: but I must observe that, at present, I examine only the results of the mercurial sulphuric mass when the operation is stopped at the moment in which the whole of the

\* I make use of this denomination, given by Fourcroy to the result of the action of the sulphuric acid on mercury, before water is poured into it, because this mass is capable of containing different salts, according to the state to which it is brought, and as this expression does not designate any, it is suitable to every case.



mercury being combined, the white mass resulting from it is still covered by the acid.

In this case the acid sulphate separated by the first washings, yields a light white precipitate with muriatic acid; if after this precipitation pot-ash is poured into the liquor, there is an abundant orange precipitate. This sulphate is therefore at the same degree of oxidation as that with an excess of oxide, laying aside the small quantity which is but little oxidized, precipitated by the muriatic acid. The orange colour of its precipitate does not, therefore, depend on the absorption of atmospheric oxygen, which, however rapid it may be, could not take place uniformly through the whole mass of a precipitate at the moment at which it forms. To obtain this salt pure, without any mixture of slightly oxidized sulphate, the sulphuric mercurial mass must be dried until it disengages no more sulphureous vapours. Then the water separates an acid sulphate from the mass which is not rendered turbid by muriatic acid, and which yields an orange precipitate with the alkalis. The slightly oxidized neutral sulphate described by Fourcroy, is completely precipitated white by the muriatic acid, which is conformable with the black colour of the precipitate formed in this salt by the alkalis, and shows that the mercury is very little oxidized in it. It is known that the sulphate with excess of oxide is completely dissolved in muriatic acid. Hence it should result that the neutral sulphate alone should be slightly oxidized, and that the two others, equally oxidized, should both be much more so than the first of these salts.

With respect to the formation of the sulphate with excess of oxide which is obtained by washing the sulphuric mercurial mass, I do not think that it can be occasioned by a change of oxidation, and I form my opinion on this ground: when this mass is urged by the fire so as not to retain.

retain any slightly oxidized sulphate, it is, nevertheless, white, and the colour of the sulphate with excess of oxide is only developed by affusion of water; now this water only dissolves the acid sulphate which is as much oxidized as that with an excess of oxide: it cannot be supposed that there is an absorption of oxygen, because even before the water had been poured on it, it was soluble, without residue, in muriatic acid. It appears to me equally easy to explain the formation of sulphate with excess of oxide, when, instead of urging the mass by fire, that it may not contain any slightly oxidized sulphate, it is only brought to the point prescribed by Fourcroy, that it may furnish the three sulphates. In this state it does not dissolve entirely in muriatic acid; the greatest part forms a corrosive mercurial muriate, and a small portion of mild insoluble muriate; thus two different combinations of oxygen with mercury were already in existence, and when the water acts, it only separates them in the ratio of their affinity for sulphuric acid and of the solubility of the two combinations. I satisfied myself that these different degrees of oxidation were established in the sulphuric mercurial mass, and that if any change takes place in them, it can have no sensible influence on the results, by the following experiment, which I repeated several times with attention. I boiled three ounces (91.71 grammes) of sulphuric acid with two ounces (61.14 gr.) of mercury until all the mercury was combined; it was then transformed into a white mass, above which there was a small quantity of liquid acid. I divided the whole into two parts perfectly equal in weight; on one of them I poured muriatic acid, whose action was assisted by heat; on adding water there remained only a small quantity of a white matter on which a fresh quantity of muriatic acid did not produce any effect; washed and dried, it weighed, on the different occasions in which I repeated this experiment,

from

from 50 to 60 grains (2.65 to 3.18 grammes): on the other half of the sulphuric mercurial mass, I boiled, at different times, four litres of distilled water which I had collected; muriatic acid produced a precipitate in it which was always of less weight than that of the first half, not dissolved by the muriatic acid: all the causes which prevent this experiment from receiving the accuracy which analysis requires, will be readily perceived; I am, however, of opinion that there is enough to justify me in concluding that no appreciable change in the oxidation of the mercury takes place in the course of the washings.

The state of oxidation of the metal is entirely determined by the manner in which the operation is conducted: if sulphuric acid, diluted with an equal volume of water, is employed, the salts obtained are only slightly oxidized, insoluble in the muriatic acid, and give grey precipitates with the alkalis. I have proved that, in the method described by Fourcroy, the oxidation of the mercury had not been able to reach the point necessary to its being totally soluble in muriatic acid, and that it was requisite to heat the mercurial sulphuric mass until no more sulphurous acid was disengaged, that it might not contain any slightly oxidized mercury. In the first case, the water with which the acid is diluted, modifying the action which it exercises on the mercury, this is incapable of being oxidized as much as it would have been without this circumstance. In the second, on the contrary, no force restraining the action of the acid, the metal is more oxidized and would wholly pass, as in the third case, to the highest degree of oxidation to which it can be carried by these means, if the operation was not stopped.

The existence of the mercurial sulphates at different degrees of oxidation depending entirely on the method of operation, and the action of the water made use of not contributing to it, it is only exercised on the acid, which  
is

is at first equally combined with all the mercurial oxide, and of which it determines an unequal division; from this division results the formation of the acid and neutral sulphates, while that of the sulphate with excess of oxide is owing to its relative insolubility.

The precipitate of the acid sulphate is not a pure oxide, as is advanced by Fourcroy, but rather, agreeably to the experiments of Bayen already mentioned, a salt with excess of oxide, which, according to the remark of the same chemist, is analogous to the turbith when it is much oxidized; when it is less so, it is of a grey colour: the acid is completely carried off by an alkali, leaving the black oxide of mercury free. This experiment proves that the sulphate with excess of oxide can also exist at different degrees of oxidation.

I shall continue to make use of the name of salt with excess of oxide given by Fourcroy to the salts which Rouelle had named with *minimum* of acid, because this latter denomination seems to indicate a fixed term of combination, and I shall show that the salts with excess of oxide, though insoluble, are still susceptible of variation in the proportions of their component parts.

Vauquelin has observed\* that the muriate of lead is capable of entering into combination with a new quantity of oxide of lead, and of thus forming a muriate of lead with excess of oxide, distinguished from the common muriate, principally, by the property of taking a beautiful yellow colour by calcination: he has ascertained the existence of a nitrate and a sulphate of lead with excess of oxide.

The precipitates of the solutions of copper, so remarkable for the unexplained variations of their colours, have fixed the attention of Proust†: he satisfied himself that

\* Ann. de Chim. Tom. XXXI.

† *Ibid.* Tom. XXXII.

the green precipitates of the nitrate, muriate, sulphate and acetate of this metal are salts with excess of oxide the proportions of which he determined : the analyses of several of these salts gave me results similar to his. With respect to the blue precipitates of the same solutions, Proust considers them as a particular species of compounds formed by the combination of water with the oxide of copper, to which he gives the name of *hydrate of copper*. I shall prove in the course of this work that this opinion is not well founded, although Chenevix has endeavoured to support it by facts, otherwise interesting. Klaproth has discovered \* that the precipitates formed by water and alcohol in the muriate of tellurium, always retain some acid, so that they may be classed among the salts with excess of oxide.

Lavoisier †, who, of the experiments quoted, could only be acquainted with those of Rouelle and Bayen, presumed that the metallic oxides retained some of the acid with which they were combined, and of the precipitate made use of in their separations from their metallic solutions. It has been since proved ‡ that *the chemical action of metallic solutions is subject to the same laws as that of other substances, unless the oxidation occasions a variation in the affinity of the metal either for the acids, or for the other substances, and multiplies, as it may be said, the property of forming combinations, in the metals*. The applications of this principle gives the theory of the different phenomena hitherto observed in the metallic solutions. It more especially results from this that *when a metallic combination is decomposed, the alkali or the al-*

\* Extrait du 3<sup>e</sup>. vol. des analyses de Klaproth. Ann. de Chim. Brumaire, An XI.

† Opusc. phys. et chim. p. 247.

‡ Recherch. sur la loi des affin. Mem. de l'Institut. Tom. III.



*kaline earth employed, makes a division of the acid, in proportion to the energy of its action, which gives rise to salts with the least acid. If the metallic combination is weak, water alone is sufficient to decompose it, and salts are then also formed with the most or the least acid; sometimes also the oxide divides the precipitant with the acid, sometimes the precipitant, the acid, and the metallic oxide form two complex combinations, one of which is insoluble, and the other remains liquid.*

All the observations hitherto collected, as well as those which I have just detailed, prove the accuracy and the truth of these consequences.

I have endeavoured to estimate, as far as I was able in each experiment, the state of oxidation of the metal. It is true I only offer comparative valuations; but besides being sufficient for the interpretation of the phenomena, it would have been impossible, in the greatest number of instances, to have acquired absolute data; for this property of the metals of combining with different quantities of oxygen, is one of the causes which contribute most to produce a variation in their affinity for the acids, as well as in the results of the combinations, and, at the same time, it is one of the most difficult to determine, from the facility with which the different degrees of oxidation succeed each other in most of the metals. Tin, to which I shall now proceed, furnishes more than one example.

To appreciate the oxidation of tin, I made use of the two well known properties possessed by its solutions: the one is that of giving black-brown, or golden-yellow precipitates with hidro-sulphuret of pot-ash, according as the metal is at the weakest or at the strongest degree of oxidation; the intermediate shades between these indicate the mean degrees. The other is that of forming a black precipitate with the oxygenated muriate of mercury when the tin is but little oxidized, and a white one, if it is more

so, while, when this metal is at a still higher degree of oxidation, its solutions do not produce any effect on the oxygenated muriate of mercury.

Thus a slightly oxidized muriate of tin precipitates the oxygenated muriate of mercury black, and gives a precipitate of the same colour with hidro-sulphuret of pot-ash.

The crystals of muriate of tin dissolve in distilled water, rendering it milky, and a considerable precipitate is soon formed in it, if much less muriate of tin has been put into the water than is required for its saturation. The solution gives signs of acidity.

The precipitate collected and washed with the greatest care in distilled water offered the following characters :

A. It re-dissolves with facility in muriatic acid, and is precipitated black by oxygenated muriate of mercury and hidro-sulphuret of pot-ash.

B. Nitric acid diluted with water dissolves it, and precipitates nitrate of silver.

C. A weak solution of caustic pot-ash deprives it of its white colour and it takes a deep grey ; the alkali saturated with nitric acid, precipitates the nitrate of silver.

D. By distillation in an open fire, it gives some vapours of muriate of tin, and afterwards muriatic acid : a grey oxide is found in the retort.

This precipitate is therefore a muriate of tin with excess of oxide, in which the metal is at the same degree of oxidation as in the acid muriate which remains in solution : the true colour of this oxide is a deep grey.

The separation of this muriate with excess of oxide appears to me to be easily explicable in this case. It is, in fact, proved that the oxide of tin tends to form two combinations with the muriatic acid, the one insoluble, in which the oxide predominates ; the other soluble, and with an excess of acid. The action of water on the muriatic acid

acid favours the formation of this, while the natural insolubility of the first contributes to its separation.

When the quantity of muriate of tin is small compared with that of the water made use of, the water, whose action is augmented by its quantity, abstracts the acid from the combination which existed, and the muriate with excess of oxide separates. By adding to this solution nearly as much muriate of tin as is necessary to saturate it, the lower part of the liquid, being in contact with the salt, becomes limpid; only that part remains milky in which the water predominates, until the quantity of oxide of tin held in solution forms an equilibrium with that of the water, then the insoluble muriate resumes the acid which the water had deprived it of. In this state it has also an excess of acid like all the solutions of tin; kept in a bottle with a ground stopper, and filled, it gives, in a short time, a white precipitate, because the two causes which I have already noticed, still act, though they are greatly limited by the mass of oxide of tin. The separation which takes place in this instance, and, in general, all those which are produced by water, without a change of oxidation, are therefore to be attributed to the action which the water exercises on the acid,

The solutions of pot-ash, soda, ammonia, barites, strontian, and lime only take that quantity of muriatic acid from the oxide of tin, which is requisite to form a soluble combination, when they act in the cold, and there is not an excess of these solutions poured into the muriate of tin. The precipitate is not then an oxide of tin, as it is believed to be, but a muriate with excess of oxide similar to the preceding: it is frequently decomposed by ablutions in the cold, but more certainly with heat; the water which has been employed in this decomposition reddens turnsole-paper, and yields a black precipitate with hidro-sulphuret of pot-ash; it therefore holds an acid muriate of tin in solution.

solution. The colour of the precipitate is changed from white to grey. The oxide is not, however, yet deprived of all the acid with which it was combined, for by dissolving it in nitric acid diluted with water, it renders nitrate of silver turbid. If an excess of alkali is put into the muriate which is precipitated, the excess dissolves a little oxide of tin: the liquor separated from the precipitate, and saturated with muriatic acid, is precipitated brown by the hidro-sulphuret of pot-ash, and precipitates the oxygenated muriate of mercury white: but when instead of separating the precipitate from the supernatant liquor, the action of the alkali is assisted by heat, it carries off the acid of the precipitate, which becomes a deep grey. By suffering the alkali to act in the cold, there is only a slow and partial decomposition. The reagents do not indicate any change in the degree of oxidation of the oxide, freed, in this manner, from every combination.

Proust observed\* that when muriate of tin was decomposed by pot-ash, this alkali redissolved all the precipitate which was formed, if a sufficient excess was made use of, and that, in this solution of oxide of tin by pot-ash, a sort of metallic cauliflower (*choufleur metallique*) was formed in a short time, which he took for revived tin, after having ascertained that the portion of oxide which remained in solution had no longer the power of changing corrosive sublimate. It is known† that pot-ash dissolves highly oxidized tin more readily than that which is but little so: now, the united affinities of oxide of tin for a new quantity of oxygen, and of pot-ash for the metal brought to this state, are sufficient to destroy the uniformity of its oxidation. One part of the oxide forms a permanent

\* Recherch. sur l'Étain. Journ. de Phys. Fruct. An. VIII.

† Obs. sur l'acide de l'Étain, par Guyton. Ann. de Chim. Tom. XXIV.

combination with the alkali, by taking oxygen from the other part which precipitates slowly and collects in the form of a metallic herborization of a black-grey colour, and which still retains a sufficiency of oxygen to be soluble in muriatic acid in the cold, without effervescence. This oxide has a metallic lustre which doubtless arises from the symmetrical arrangement of its particles. By boiling a solution of pot-ash on a greater quantity of the oxide precipitated from a muriate than it is capable of dissolving, the division of the oxygen takes place more quickly: the degree of oxidation of the metal dissolved by the alkali is raised, as in Proust's experiment, and that which is not dissolved is in the same state as that precipitated in this experiment.

The energy with which pot-ash tends to raise the oxidation of tin by dissolving it, is such, that when only a small excess of alkali is put into the muriate of tin which is decomposed, the small quantity of oxide held in solution is more oxidized than it was in the muriate, as is proved by the colour of the precipitate furnished by the oxygenated muriate of mercury.

The six alkaline substances mentioned above, dissolve the oxide precipitated from the muriate of tin, in a greater or less quantity according to the intensity of their alkaline property; none of them appeared to me to form an insoluble combination with the muriate with excess of oxide, but they all formed soluble triple salts characterized as follows:

The muriate of tin and pot-ash crystallized in rhomboidal prisms, terminated at the two extremities by two truncatures corresponding to the great angles of the prism; it is remarkable that the muriate of ammonia and tin, and that of tin and barites, affect exactly the same form. The muriate of tin and soda, as well as that of tin and strontian, crystallize



crystallize in fine needles. The muriate of tin and lime is deliquescent, and crystallizable with difficulty.

Thus the conjecture of Cit. Thenard\* respecting the existence of muriate of ammonia and tin is verified : it is probable that had he carried his experiments farther he would have discovered in pot-ash, soda, and the other salifiable bases the property of forming triple metallic salts which he thought did not belong to them.

The carbonates of pot-ash and soda precipitate the muriate of tin with a brisk effervescence which might at first be attributed to the excess of acid which always accompanies the solutions of tin, but it continues until the complete decomposition of the metallic salt, and the precipitate redissolves in the acids without the least disengagement of carbonic acid: by this means, therefore, a muriate with excess of oxide is formed, and not a carbonate of tin.

I shall also remark on this subject, that when the muriate of tin is decomposed by an alkaline substance, the first effect of the precipitant is not, as might be supposed, that of saturating the excess of acid natural to this salt: on the contrary, however far the precipitation may be advanced, the liquor gives signs of acidity as long as it holds tin in solution. This remark, which I believe has not been made on any acidulous salt, proves that the acid indicated by the reagents, far from being considered as free, and, in some respect, superabundant in the combination, is retained by the affinity existing between it and the insoluble salt, to which it communicates the property of dissolving in water. The action of an alkali on the solution of a similar salt, is therefore confined to depriving the salt with excess of oxide of the acid which held it in solution, and this preci-

\* Not. sur les différ. comb. du cobalt avec l'ox. suivie de plusieurs obs. sur les sels ammoniac. métal. Ann. de Chim. Flor. An. X.

pitates in proportion as it is freed from the quantity of acid which rendered it soluble.

I have verified this observation in the other salts of tin of which I shall speak, in those of lead and in several combinations of iron and copper; I believe it may be extended to all the metallic solutions which require an excess of acid, or, in general, to substances which can form two species of compounds with the acids, the one soluble, and which still retains acid characters; the other insoluble, and in which the acid, from being in a smaller quantity, is completely neutralized.

The strong affinity of tin for oxygen renders its solution in nitric acid very difficult. Pelletier has proved that the salt obtained by Bayen, by treating tin with the concentrated acid, and which he named *stanno-nitrous salt*, is nitrate of ammonia, and does not contain the metal.

This observation, added to those which follow, seems to me also to destroy the opinion of Cit. Thenard\*, on the solution of highly oxidized tin in nitric acid, by the aid of ammonia.

Bayen, however, succeeded in dissolving a small quantity of tin, by Kunckel's process, described by Rouelle. By employing nitric acid diluted with water, and by operating with heat, as was done by Cit. Guyton, the acid and the water are decomposed; gaseous oxide of azote and nitrate of ammonia are obtained, and the tin, being too strongly oxidized, is not dissolved. Proust in his *Inquiries concerning Tin*†, has indicated the process by which he succeeded best in forming nitrate of tin. It consists in using nitric acid of 150. ; in plunging the vessel in which the solution is made into cold water, to moderate the heat which is produced; and, in putting in the metal by small portions.

\* Ann. de Chim. Flor. An. X.

† Journ. de Phys. Fruct. An. VIII.

A solution of tin is obtained of a yellowish colour, containing ammonia, and in which the tin is not more oxidized than in the muriate, since, like this, it precipitates the oxygenated muriate of mercury, black: this solution yields a white precipitate spontaneously, which is much increased by heating it, and all the metal may be precipitated from it in this manner, without a crystallization being obtained. The precipitate which Proust took for oxide of tin is a nitrate with excess of oxide, from which pot-ash carries off the acid and causes the oxide to reappear of the grey colour which is natural to it: it also resumes it in distillation, and exhales ammonical vapours. A solution which has the same properties as these, is formed by dissolving the oxide precipitated from the muriate of tin, in nitric acid diluted with water. The alkalis separate a nitrate with excess of oxide from both these solutions, similar to that which precipitates spontaneously. The white oxide, formed by the rapid action of nitric acid on tin, does not give any indication of solution in this acid; the alkalis dissolve it abundantly and without changing its colour. When this solution is a little concentrated, it takes a gelatinous consistence such as is observed in the oxide which is separated from the nitro-muriate of tin. Distillation gives a yellow tinge to this oxide, but does not disengage either nitric acid, nitrous vapours, or ammonia. This oxide is very little soluble in the acids, and greatly so in the alkalis, while the slightly oxidized oxide combines in a manner directly the reverse.

The sulphuric acid, whether diluted in water, or concentrated, only oxidates tin with difficulty, and consequently dissolves but a small quantity; but if concentrated sulphuric acid is poured into muriate of tin, a little diluted with water, the muriatic acid is disengaged, and a white flocculent precipitate is formed, which redissolves in the water, although its comparative insolubility had determined its precipitation.

precipitation. By evaporating this solution of sulphate of tin slowly, it crystallizes in long, very slender prisms, which increase in every direction. The oxidation of the metal is not varied in this operation, and, as in the muriatic solutions, it yields black precipitates with hydro-sulphuret of pot-ash and oxygenated muriate of mercury. The precipitate formed by the alkalis, well washed and redissolved in muriatic acid, precipitates muriate of barites. By the assistance of heat, the alkalis take a portion of its acid from it; its whiteness tarnishes, but the oxide of tin seems to retain the acid too strongly for the alkali to be capable of depriving it entirely of it; it blackens in the fire, emitting some sulphureous vapours: this precipitate is therefore proved to be a sulphate with excess of oxide. By heating this sulphate of tin strongly with sulphuric acid, the acid is decomposed by the slightly oxidized tin, and sulphureous acid is disengaged. The oxygenated sulphate of tin which forms, no longer changes the oxygenated muriate of mercury; it is precipitated yellow by the hydro-sulphuret of pot-ash; it is not susceptible of crystallizing, but, by being brought to the consistence of syrup it forms, on cooling, a mass of a vitreous appearance and yellow colour, deliquescent and soluble in water, which separates a part of the oxide. I obtained this precipitate in too small a quantity to ascertain whether it retained any acid: I did not find any in that formed by the alkalis, and, from the weak affinity of the acids for highly oxidized tin, I presume that this was the case with the first.

With the alkalis, the acetate of tin gave an acetate with excess of oxide, white, insoluble, decomposable in the heat by the alkalis, and whose grey oxide is at the same degree as that of the muriate.

The most ready method of obtaining a solution of tin in acetic acid is to decompose acetate of lead by muriate of tin. In this process, employed by Hausman in the operation

tion of dyeing, besides the acetate of tin which remains in solution and the muriate of lead which precipitates, a triple salt of tin and lead is formed whenever more muriate of tin is put into the mixture than the acetate of lead can decompose. The solution of this salt contains much more lead than that of the muriate of this metal, as is proved by the precipitation of equal volumes of these two saturated solutions by sulphuric acid. It crystallizes in thin plates, of a milky white, pearly, having a resemblance to mica. These laminæ have so little consistence that on decanting the liquid in which they are crystallized, they stick to each other, and are blended without preserving any form. This salt, with two metallic bases may also be formed by the direct combination of muriatic acid with a mixture of the two metals, or of their oxides, and by digesting muriate of tin on an oxide of lead. The muriate of tin and lead, obtained in these different processes, has always an excess of acid.

I have said above that the inquiries of Citizen Vauquelin, respecting the decomposition of muriate of soda by oxide of lead, have occasioned the examination of the muriate, sulphate, and nitrate of lead with excess of oxide: to these salts I add the acetate with excess of oxide which is separated by precipitating the acetate, and, which is completely deprived of acid by the action of the alkalis assisted by that of heat, leaving a red oxide of lead disengaged from every combination.

I conclude this first memoir by collecting the consequences which appear to me to be derived from the observations I have made. 1st. The existence of sulphates of mercury, at different degrees of acidity, results from the action of the water employed in the washings: the oxidation of the metal in these divers combinations does not receive any modification from it, and is only determined by the manner of operating, which renders the action of the acid more or less powerful. 2d. The separations  
 11 2 produced



produced by the water in the metallic combinations, without a variation in the oxidation of the metal, are owing to the action of the water on the acids. 3d. The excess of acid indicated by the re-agents in certain salts, is the cause of their solubility, and when it combines with a substance which has more affinity for it than the insoluble salts have, this separates. 4th. The property of metals, of forming triple salts, is not limited to those resulting from the union of the same acid with a metal and an alkali ; it appears to extend to the results of the combination of one acid with two different metals. 5th. Finally, the precipitates formed by the alkalis in the solutions of tin and lead, are salts with excess of oxide.

*Continuation of Observations on the Precipitates of Metallic Solutions, read at the Sitting of the 12th Floreal.*

I mentioned in my first memoir that the green precipitates of copper, that is to say, those which are always obtained when the metal held in solution is not completely precipitated, have been considered by Proust\* as salts with excess of oxide, the proportions of which he has determined. He has observed, that as soon as they approach the term of complete precipitation, the precipitate acquires a blue tint, which grows deeper, by adding an excess of alkali; and that this precipitate, already distinguished from the first by its colour, differs from it also by the following properties :

“ It has not the pulverulence of the green precipitates,  
“ but a consistence which resembles that of Prussian  
“ blue.”

\* Ann. de Chim. Tom. XXXII.

“By heating it in fine powder, spread on paper, it changes colour slowly, loses water, and is converted into black oxide. The degree of heat is not, however, sufficient to burn the paper.”

“Dry, it is unchangeable; but kept under water, it grows darker, is gradually decomposed, and finishes by becoming only black oxide, after having diminished in volume. The solar light accelerates this decomposition.”

“By distillation, 100 parts of this precipitate yield 24 of water, 75 of black oxide, and about 1 of carbonic acid.”

“The acids dissolve it without effervescence.”

“Thrown into saturated solutions of the sulphate, nitrate, and muriate of copper, it resumes a sufficiency of acid to be converted into the green sulphate, nitrate, and muriate with excess of oxide.”

From all these properties, Proust concludes that this substance is composed of water and oxide alone; he consequently called it *hydrate of copper*. He endeavours, by proofs which I shall refute, to remove every suspicion as to the presence of acids and alkalis in these precipitates. The experiments which I am about to detail seem to me to prove that they constantly retain some acid; that it is to this principle that they owe their colour; and, that they only differ from those which are green, by containing a smaller quantity of it. Thus they enter into the class of salts with excess of oxide.

To ascertain whether the precipitate formed in the sulphate of copper by pot-ash retained any acid, I washed it with great care, and dried it slowly, for it is decomposed by a very slight heat; 100 parts dissolved in muriatic acid gave a precipitate of 23 parts with muriate of barites, which indicates seven parts of sulphuric acid. If pot-ash is digested on the blue precipitate it loses its colour.

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The alkali, saturated with muriatic acid, yields a precipitate with muriate of barites of the same weight as the preceding. The black oxide which remains weighs 72 parts. The blue precipitate, analyzed by this means, gives the following results; 0.72 oxide of copper, 0.07 sulphuric acid, remains for the water 0.21. By comparing these results with those given by Proust, for the green sulphate with excess of oxide, that is to say, 0.68 oxide, 0.18 acid, and 0.14 water, it will be seen that the first of these salts contains less acid, more oxide, and more water than the latter.

The differences observed between the analysis of the blue sulphate with excess of oxide, made by Proust, and that which I offer, may be attributed to those of the methods which we employed. Nevertheless, by following his, I found no greater agreement with his results. To make this analysis, Proust distilled 100 parts of this salt, from which he obtained 0.75 oxide, 0.24 water, and 0.01 carbonic acid : on repeating this experiment, I obtained nearly the same quantity of sulphuric acid, when I performed it with a gentle heat, the water which came over was not sensibly acid, but the solution of the black oxide in muriatic acid, precipitated the muriate of barites. At other times, I employed a heat capable of disoxidating the copper in part, then the last portion of the water which passed reddened turnsole-paper strongly, and the copper redissolved, gave also a slight precipitate with muriate of barites.

Finally, an observation of Proust himself adds to the evidence of the proofs which I have just given of the existence of the acid in these precipitates. He observes that they are slowly decomposed under water ; this decomposition, accelerated by light, is still more so by heat. Thus on boiling two litres of water on 60 grammes of the blue sulphate, with excess of oxide, it will be seen that  
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its colour soon tarnishes, and passes to black. The water does not give marks of acidity with the test papers, it, however, precipitates the muriate of barites abundantly. Concentrated in a retort, and brought to about  $\frac{1}{20}$  of its volume, it reddens turnsole paper. On urging the evaporation still farther, the acid concentrates; it reaches the point at which it produces the same sensation on the tongue as the sulphuric acid of commerce; and by continuing the heat, it exhales in white vapours, exactly similar to those of sulphuric acid. There remains a black spot at the bottom of the evaporating bason, arising no doubt from a small quantity of vegetable matter, separated from the filtre by the water, and on which the sulphuric acid had exercised its action: finally, this evaporation conducted slowly, and stopped at the periods most favourable for crystallization, did not give any salt. The boiling water, therefore, by depriving this precipitate of its blue colour, only carries off its sulphuric acid.

The decomposition of the blue sulphate with excess of oxide is never complete by this process, however often the ablutions in boiling water may be repeated. It loses its blue colour by the first ebullition, and appears brown, but it becomes a bluish grey as it dries. In the subsequent washings it turns more and more to brown, and the water always acquires the property of precipitating muriate of barites.

I boiled five litres of water on 60 grammes of blue sulphate with excess of oxide, in five portions; the water of the last precipitated muriate of barites, as I have mentioned, and the residue, dissolved in muriatic acid, also gave a precipitate with this reagent.

The blue precipitates of the nitrate and muriate of copper, exposed on burning coals, exhaled vapours, which, as well as those disengaged by the action of concentrated sulphuric acid on the same precipitates, indicated the presence

presence of the nitric and muriatic acids. To show that the latter acid is contained in the blue precipitate of muriate of copper, it is sufficient to observe that if it is dissolved in nitric acid, the solution will precipitate that of silver.

If these experiments establish, as it appears to me they do, that these precipitates contain acid, they also destroy the objections which Proust opposes to this opinion. I believe they render it unnecessary for me to refute those which he deduces, because *pot-ash, which does not spare the carbonic acid of the metallic carbonates, even when it is not entirely caustic, will not, for a stronger reason, admit of any of the other acids, and because it seizes all the acids which it meets with, with extreme avidity.*

It might be supposed that these precipitates, besides the acid, retain a part of the alkali employed to separate them, and it may be found that Proust's analysis, which he adduces in opposition to this opinion, is not sufficient to show its falsity; but it seems to me that if, for example, the blue sulphate with excess of oxide had contained any alkali, the water must have separated a sulphate which would have crystallized during the evaporation. The blue nitrate, with excess of oxide, urged by fire in a crucible with a little charcoal, did not give any trace of an alkali. These experiments confirm the assertion of Proust.

Chenevix, in admitting the hidrate of copper, has endeavoured to support it by several experiments, inserted in a memoir\* on the analysis of the arseniates of copper and iron. The name of the author, and the nature of the proofs he brings, might yet occasion doubts if they were not refuted in a convincing manner.

Although struck with the impropriety of the denomination of hidrate of copper, given to the blue precipitate of

\* Philos. Trans. 1802.



this metal, Chenevix adopts it. He himself blends the blue and green precipitates under this name, without attending to the saline nature of the latter, which has been well determined by Proust. He believes that the blue and green colours of the solutions of copper are owing, like those of their precipitates, to the combination of water and oxide of copper; whence it results, according to him, that these coloured solutions are not combinations of acid and oxide of copper, but of acid with the hidrate, or with the oxide united to the quantity of water requisite for it to pass to the state of hidrate: so that to give an exact idea of the composition of the salts of copper, he directs the quantity of acid, the quantity of water of crystallization, the quantity of oxide, and that of the water which constitutes it a hidrate, to be specified.

Proceeding on this idea, Chenevix affirms that *if sulphuric acid diluted with water is poured on the brown oxide of copper, a salt is obtained which exceeds, by 24 per cent. the quantity which would have been obtained by employing the green precipitate*: he explains this by saying, that *the first operation of the oxide is to take the quantity of water which is necessary for it to become a hidrate, and that the combination of the sulphuric acid takes place, not with the oxide, but with the hidrate.*

An attentive examination of the results of this experiment inspires me with some doubts as to its perfect accuracy: 100 parts of hidrate of copper, according to the data of Proust, adopted by Chenevix, contain 75 of black oxide of copper. Now, 75 of oxide of copper form 235 of sulphate of copper\*, and 100 parts of oxide, 313 of sulphate. The difference of these products is 78: the 25 parts of water combined in the first instance in the pretended hidrate, being found in both these products, their

\* Ann. de Chim. Tom. XXXII.

real difference is only 78—25 or 53. But Chenevix, instead of making use of the blue sulphate with excess of oxide, says expressly that he employed the green substance, in which the latter chemist discovered only 68 of black oxide, and which, consequently, would only have given 213 parts of sulphate of copper. The difference between the quantities of this salt produced by the combination of sulphuric acid with 100 parts of oxide, or with 100 parts of green sulphate with excess of oxide, is therefore 100 parts, *minus* 32 of water and acid combined with the oxide, of which the green substance is precisely 68 parts of sulphate of copper, and not 24, as is said by Chenevix. It is probable that, relying on the theory which he had formed, he gave but little attention to this experiment; which, even supposing that it was exact, does not disprove the existence of the acid in these precipitates, nor does it in any manner demonstrate the nature of the hydrate, such as it is supposed by Proust.

Chenevix observed that *the muriate of copper, gently concentrated, changed its bluish-green colour into a fine brown, which, by cooling or by the affusion of water, resumed its primitive colour*, and he draws a conclusion from this fact in favour of his theory, by saying that *the brown liquor is a solution of muriate of copper, while the green liquor, like all the blue or green solutions of copper, is a combination of muriatic acid with hydrate of copper, or a muriate of hydrate of copper*. He also acknowledges that he was unable to produce these changes of colour as often as he wished. Every thing which I have hitherto said seems to me to destroy the theoretic consequences deduced from this phenomenon; but since its true causes have not been pointed out, and they are not devoid of interest, I shall give some explanation of them.

On concentrating a solution of green muriate of copper, its colour grows darker, and becomes so intense, that it  
appears

appears nearly black. Nevertheless, on agitating the liquid in the evaporating capsule, the edges which it impregnates are tinged of a deep bottle-green if the vessel is of glass, and of a yellow-green if it is porcelain. The solution does not experience any change: water does not render it turbid, it only brightens its tint, and if it is in sufficient quantity, brings it to a very pale bluish-green colour. I therefore am of opinion that the author of the analysis of the arseniates of copper and of iron did not indicate correctly the colour he obtained in the experiment which he relates.

Whenever a solution of copper is really brown, water occasions very remarkable changes in it. It produces a white precipitate in it, and on putting but a small quantity of water into it, the liquor retains only a bluish tint of little intensity. In this precipitate the slightly oxidized white muriate of copper, described by Proust\*, will be readily recognized: the blue colour of the liquor shows that it holds a more oxidized muriate of copper in solution. The circumstances in which the muriatic solutions of copper become brown, furnishes the theory of the separation of these two differently oxidized muriates, produced by the water.

If copper is treated with muriatic acid in closed vessels, the solution is without colour; water precipitates the metal completely in the form of white muriate. By exposure to the air this solution takes, at first, a light tawny colour, which becomes brown, and will pass to green if it is left for a sufficient length of time. When it is brown, water acts upon it in the manner I have mentioned above.

According to Proust, copper scales contain about 27 per cent. of metallic copper, the rest is oxidized to 25 per cent. If, therefore, concentrated muriatic acid is poured on

\* *Recherch. sur l'Etain. Journ. de Phys.* 1800.

them, there is an effervescence, and a production of heat, and the solution is almost instantaneously of a very deep brown.

The chemist whom I have just cited has made known the property possessed by the muriate of tin of partly dis-oxidating the muriate of copper, and causing it to pass to the state of white muriate, little oxidized and insoluble. By mixing a sufficient quantity of solution of tin with the muriate of copper, all the copper may be separated in this manner\*. If the solution of tin is only poured drop by drop into the muriate of copper, the white muriate formed by each drop, is redissolved by agitation: the colour of the liquor becomes a deeper and deeper green, and finally, before the precipitate is permanent, has acquired an intense brown colour without any mixture of green. The action of water on the muriate of copper, brought to this state, is the same as on the other brown solutions.

The different modes of producing a brown muriatic solution of copper show that the metal is in an intermediate state of oxidation, greater than in the white muriate, and below the green muriate, in which the metal appears to be combined with all the oxygen which it can saturate. Water poured into a brown solution of copper, at first takes acid from the metal, and determines a new order of combination between the oxygen and it: a part of the metal is, at once, deprived of the acid necessary for its solution and of the oxygen which is superfluous in the formation of the white muriate; the other part of the copper remains in solution combined with the oxygen, which constitutes the difference of the state of the metal, in the white muriate, from that in which it was when it formed a brown solution; thus super-oxidized, it gives the green colour to its

\* Recherch. sur l'Etain. Journ. de Phys. 1800.

solution, which all those have in which the copper is oxidized to 25 per cent.

The division of acid which takes place occurs in too many instances to leave any doubt as to admitting it. The precipitation of white muriate, observed by Proust, when water is poured into a slightly oxidized muriate of copper, whose acid is saturated with oxide, is also owing to it. An excess of acid redissolves the precipitate and deprives the water of the faculty of reproducing it: the white precipitate is therefore a muriate but little oxidized, with excess of oxide. I have related several analogous facts.

Although the circumstances in which the brown solutions of copper are formed determine the state of oxidation of the metal, and the brown colour of these solutions shows that they are not a mixture of two solutions of copper, one little oxidized and without colour, the other green and greatly oxidized, there may be some hesitation at first in admitting the division of the oxidation as instantaneously produced and resulting from the action of the water on the acid; but though these doubts appear to me to have but little foundation, I am of opinion that they will be removed by its approximation to several similar phenomena; of this description are the division which takes place in the oxidation of slightly oxidized tin, dissolved in pot-ash; that produced by sulphuric acid in the white muriate of copper with excess of oxide, from which it results that the copper being uniformly oxidized at 16 per cent. a part of the metal is completely revived, while the other, brought to 25 per cent. of oxidation, is dissolved by the sulphuric acid\*; and that which, according to Chenevix, is produced in the same manner on copper oxidized to  $11\frac{1}{2}$  per cent. by phosphoric acid.

From what I have now advanced both on the solutions of copper and on their precipitates, it results, 1st, That

\* Proust, Journ. de Phys. 1800.



the blue precipitates are salts with excess of oxide, containing less acid than the green salts with excess of oxide: the water which enters into their composition is no otherwise combined than in other saline combinations. 2d, That the copper is not limited in its combinations to the two degrees of oxidation determined by Proust: it takes others, which readily return to the two extremes. This opinion, in opposition to his doctrine, is conformable to what takes place with several other metals, and particularly with tin, in which I may point out four different states; that in which its solution does not change that of oxygenated muriate of mercury; that in which it precipitates it black, and in which the oxide is grey; finally, that to which this latter oxide passes when, being partly dis-oxidated by the action of pot-ash, it acquires a sort of metallic lustre\*. I do not, however, assert that each of these states indicates a constant degree of oxidation. 3d, It also results, that the white precipitate formed by water in the slightly oxidized muriate of copper, is a slightly oxidized muriate with excess of oxide. According to Proust, this salt loses acid by the action of boiling water; it becomes brown, and, in this state, it appears to me to be, to the white muriate with excess of oxide, nearly like what the blue salts with excess of oxide are to the green salts with excess of oxide.

It appears to me that it would be more difficult to show the differences between the blue and green solutions of copper than those of the uncoloured solutions and the brown. It might be believed at first that they are equally

\* Though probably, from an oversight in printing the work, there are but three states of oxidation specified here, a reference to page 474, will show that this intelligent young chemist had observed a fourth state, in which it precipitates the oxygenated muriate of mercury *white*. T.

produced by that of the oxidation, for the solutions in which the copper is most oxidized, such as the oxygenated sulphate, nitrate, and muriate, are constantly of a blue colour, and those in which the metal may be supposed to be least oxidized, as in the muriate and acetate, are most commonly of a green colour; but on making the latter solutions with the oxide precipitated from the first, their colour is still green. Some solutions of copper take sometimes one and sometimes the other of these colours: blue crystals are sometimes observed to form in the midst of a green solution: whatever their colour may be, these solutions have always an excess of acid.

The facility with which the oxidation of copper varies, which seems to me to determine the difference between the white, brown and green colours of these solutions, and not to have any influence on those which are coloured blue or green, also explains the utility of this metal in the *reserves* (Fr.) employed in the art of printing on linen. The name of *reserves* is given to the compositions intended to prevent those parts of the stuff, on which it is applied, from being coloured in the indigo vat, made by means of sulphate of iron and lime. The receipts, more or less loaded with useless articles, which are followed in manufactories, all prescribe verdigris and sulphuric acid, or sulphate copper. Although the advantage of these solutions of copper is well known in the reserves, yet as this metal fixes certain colouring principle, its application on linen is attended with inconvenience when the blue dye is to be followed by some operations of dyeing: it would therefore be of importance to find a substitute for it in these circumstances. The known properties of sulphate of zinc, and in particular that of not acting as a mordant, seemed to render it fit for this purpose, which, however, it accomplished very imperfectly. If three specimens are put into the indigo-vat, of which one has not received any preparation,  
another

another has been impregnated with sulphate of zinc, and the third with sulphate of copper: the first comes out green; washed and exposed to the air, it takes a blue whose intensity depends on the strength of the vat and on the time it has been in it: the second also comes out green, but washing carries off almost all the disoxidated indigo on its surface, and it retains only a faint tinge of blue: finally, the third comes blue out of the vat, and becomes white by washing. It is evident that the sulphate of zinc, decomposed by the lime which held the disoxidated indigo in solution, is able to preserve the linen, in a great degree, from the contact of the dissolved indigo, and that the effect is more complete with sulphate of copper, because, at the instant at which the decomposition of this salt takes place, the indigo precipitated from its solution is oxidated at the expense of the oxide of copper, and thus is unable to fix on the cloth. This observation shows the importance of only employing sulphate of iron very free from sulphate of copper, to raise the vats either for deep blues (*bleus curvés*) or for pale blues (*bleus fayancés*).

Proust, whom the interest of science has rendered so severe towards others, will perceive in the contradiction I offer him, only a motive similar to his own. It appears to me that he was in error in advancing that *pot-ash, either saturated or caustic, dissolves hidrate of copper*: saturated pot-ash, or the carbonate of pot-ash alone has this property; this carbonate forms a triple salt with oxide of copper, the crystallization, properties, and proportions of which have been described by Chenevix\*. With respect to the caustic pot-ash, Vauquelin had shown†, previous to Proust's work, that it could not dissolve the oxide of copper, at least at the degree of its oxidation in the green muriate, nitrate, and sulphate of copper. The analysis of

\* Philos. Trans. 1802.

† Ann. de Chim. Tom. XXVIII.

brass also gave him an opportunity of ascertaining that the blue and green colours are accidentally communicated to the oxide of copper, which is naturally brown.

Most of the solutions of iron gave me salts with excess of oxide either by the action of the alkalis, or by that of water, or by spontaneous precipitation. To satisfy myself as to the nature of these precipitates, I employed processes analogous to those which I have already described, and these experiments are so simple that I need not dwell upon the details of them. In general, the precipitates of the very oxidized sulphates, like those of the red sulphate, the nitrate made very rapidly, and the greatly oxidized oxalate, do not retain any acid, or only a very small quantity: the precipitates of the slightly oxidized sulphates, on the contrary, are almost always salts with excess of oxide. In the first, the red colour of the oxide predominates; the second are coloured with different shades of yellow. Pot-ash carries off the acid from these salts, and deprives them of their colour, leaving the black oxide of iron at liberty in the latter, and the red oxide in the first: the colour of the precipitates cannot, therefore, be depended upon in judging of the state of oxidation of the metal in these solutions. The green sulphate of iron, or still better, the slightly oxidized acetate formed by the decomposition of acetate of lead by sulphate of iron, is employed in the fabrication of pencilled linens to obtain the colour called yellow rust of (*jaune de rouille*). The salt, with excess of oxide, which forms on the cloth, has an agreeable yellow which is tarnished by the contact of alkalis turning grey; it afterwards becomes red by exposure to the air: the cause of this effect of the alkali is, that the black oxidé, deprived by it of part of the acid which it saturates, appears then in its natural colour, which turns red as the metal oxidates by the air. The change of the yellow colour of the spots of iron-mould

by the action of very concentrated leys, is therefore not to be attributed to dis-oxidation, as was thought by Roard\*.

What precedes shows that the quantity of acid retained by the metal modifies the shades and assists the state of the oxidation of the iron, whose influence in dyeing yellow has been so well made known by Chaptal†.

The oxalate of iron observed by Bergman is an oxalate with excess of oxide in which the oxide is black. By causing the oxalic acid to act on iron-filings, an oxalate with excess of oxide is formed and a solution of iron obtained, which, however the operation may be prolonged, is always acid. This acidulous oxalate of iron crystallizes in flat rhomboidal prisms, unalterable by the air. If oxide of iron, recently precipitated from a slightly oxidized solution, is put into oxalic acid, much oxalate with excess of oxide is formed, and when only the quantity of oxide which is nearly requisite to saturate the acid is made use of, a soluble neutral oxalate of iron is obtained, whose crystals are formed of two quadrangular pyramids placed base to base, and of which all the summits are truncated. The acidulous oxalate of pot-ash, digested with iron-filings, produces a triple salt described by Roard; but if the quantity of iron is greater than can be dissolved by the acid which is discoverable by re-agents in the acidulous oxalate of pot-ash, the iron continues to abstract the acid from the pot-ash in the ratio of its mass, and the liquor gives indications of alkalinity. Filtered and evaporated, the free alkali, whose action is no longer opposed by that of the iron, in its turn, takes the acid from the dissolved metal: oxide of iron is precipitated; the liquor becomes neutral, and, by cooling, yields crystals of oxalate of pot-ash and iron, formed of green laminae placed on each other.

\* Ann. de Chim. Tom. XL.

† Mém. de l'Institut. Tom. III.



The facts collected in these two memoirs, independently of the particular inferences which I have drawn from several of them, prove the generality of this principle: when a metallic combination is decomposed, a division of the acid is made, in proportion to the energy of the substance employed; hence arise the salts with excess of oxide. As in the other chemical phenomena, the proportions of these compounds are the result of the quantity of the substances brought into action, and of the other circumstances of the experiment, which, sometimes, produce fixed proportions.

FINIS.

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